IDENTIFICATION OF CHEMICALLY-SPECIFIC REACTION SITES ON COAL SURFACES - PHASE II

BY

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SUMMARY

This report examines the low temperature oxidation of coal. Oxidation was carried out using $^{18}O_2$ as well as OsO_4 and Fe^{3+}. The progress of oxidation and the generation of organic functional groups on the coal surface as a result of the oxidation process was followed using a variety of techniques including SIMS, XPS and SEM. SIMS imaging has been especially useful when site specific reagents have been applied to the coal surface since the surface distribution of elements is indicative of both surface functional groups and sites associated with inorganic mineral matter of catalytic activity. XPS and SEM provide results complimentary to those obtained from SIMS analysis thus aiding and extending the interpretation of the SIMS results.

The data obtained show that SIMS in conjunction with $^{18}O_2$ oxidation of coal provides a good measure of both the activation energy for adsorption of O_2 on the coal surface and that of the subsequent oxidation reaction. In addition the initial oxidation is seen to be localized in regions which are already oxidized and/or proximate to aluminosilicate mineral matter.

OsO_4 has been shown to be a useful site specific reagent capable of probing the oxidation mechanism in coal and identifying sites especially prone to oxidation.

Finally the reaction of Fe^{3+} with coal surfaces in the presence of $Fe(CN)_6^{3-}$ has been investigated. The results show that the development of an intense blue color associated with a charge transfer complex between Fe^{2+} and Fe^{3+} (Prussian Blue). The kinetics of the reaction can be followed by colorimetry and are directly related to the O/C ratio of the coal. This provides a good measure of coal rank and possibly of its coking and thermal properties.

Chapter 1

STATEMENT OF WORK

Background

Secondary Ion Mass Spectrometry has been developed as a sensitive analytical technique for studying the low temperature oxidation of coal. Our recent work has extended the use of SIMS to include a number of specific derivatization reactions which have proved to be of value in studying both specific oxidation mechanisms and the distribution of functional groups in coal. Specifically we have used the Cameca IMS-3f Ion Microscope at Surface Science Western to examine the activation energies for both uptake and desorption of oxygen from vitrinite macerals in a series of preselected coals. In addition we have examined the distribution of products on coal surfaces after specific sequences of reactions aimed at revealing the distributions of functional groups at competing sites.

This work has been extended to include other complementary techniques such as X-ray Photoelectron Spectroscopy, Auger Spectroscopy and Scanning Electron Microscopy which can be used either to determine the success of individual surface reactions prior to SIMS analysis or to enhance our understanding of the SIMS results by providing data on the oxidation states of surface atoms revealed by SIMS.

This phase of the work will seek:

Tasks

1. To measure the activation energy for oxygen consumption by different macerals in four Canadian coals.
2. To study the distribution of reaction products in at least two different coals following treatment of the coal surface with CD_3I, Tollen's reagent, Rb(OH) and Ti(acac) after reaction with $^{18}O_2$.
3. To extend the reagents used to other chemical oxidants such as H_2O_2.
4. To examine the role of free radical scavengers in preventing oxidation using $^{18}O_2$ as an isotopic tracer to monitor the oxidation process.

Chapter 2

INTRODUCTION

Coal is well known as a highly reactive species. As a result its physical and thermal properties deteriorate rapidly on exposure to air. We have prepared a series of earlier reports[1-4] which have shown that SIMS is an especially powerful tool for studying both the minerology and organic function group distribution within individual coal macerals. The technique, combined with other surface sensitive instruments, such as XPS, has advanced our understanding of the geochemistry of coal.

This work was extended in our last report[4] to include a series of site specific reactions which have allowed us to determine activation energies for low temperature oxidation, using $^{18}O_2$ and to inhibit oxidation using ascorbic acid as a free radical scavenger. These results proved to be supportive of a free radical chain reaction mechanism for the oxidation of coal.

Site-specific surface reactions have been used extensively to probe the coal surface including reaction with Tollen's reagent, Rb(OH), CD_3I and Ti(acac)[10,11]. These reagents employed both individually and in sequence have been used to confirm an oxidation mechanism consistent with adsorption of O_2 on the coal surface followed by free radical oxidation.

In this study we have used $^{18}O_2$ oxidation in conjunction with SIMS to measure the activation energy of the oxidation reaction. The work also shows that the activation energy varies considerably between different sites on the coal surface. As well the ^{18}O uptake by the coal is strongly correlated with the presence of aluminosilicate minerals.

Further OsO_4 has been examined as a potential site-specific reagent while the role of Fe^{3+} as an oxidant in coal has been considered. The results suggest that while OsO_4 is of limited use reduction of Fe^{3+} by coal can be followed colorimetrically and thus provides a simple, direct measure of coal reactivity.

The report is thus divided into three main sections: Oxidation with $^{18}O_2$, derivatization with OsO_4 and oxidation with Fe^{3+}.

Chapter 3

OXIDATION WITH $^{18}O_2$

1. Introduction

The activation energy for the oxidation of coal has been studied by other authors[5-8]. We have combined oxidation by $^{18}O_2$ with the isotope sensitive analytical capability of SIMS to improve and extend these measurements[4,9]. In this work we use SIMS to measure differences in the activation energy of oxidation at different sites on the coal surface.

2. Experimental

Samples were cut from selected coals using a diamond saw. The resulting faces were polished with diamond grit and finished on a silk wheel using water as the sole lubricant throughout. SIMS analysis was carried out using a Cs^+ primary ion beam at 100 nA current and 7.5 keV net energy rastered over a 400 micron area while negative secondary ions were collected from a central area 250 microns in diameter with 100 V offset on the sample holder to suppress molecular secondary ions.

The coal samples were treated as follows:

a) Oxidation under water with $^{18}O_2$:
Coal P804 was placed under 2 mL of water, which was sufficient to just cover the coal. The vessel was evacuated and the head space was filled with sufficient $^{18}O_2$ to achieve a pressure of 0.2 atmospheres at 70°C. The system was maintained at this temperature for 48 hours then the coal was removed, dried at 105°C for two hours and subjected to SIMS analysis.

b) Oxidation under $^{18}O_2$:
   i) Samples of P804 and P832 were maintained in 0.2 atmospheres of $^{18}O_2$ at 70°C and 104°C for four days and then were subjected to SIMS analysis.
   ii) A second set of samples including P804, P832 and a new coal KG15 was treated under the same conditions for 5 days at 72°C and 104°C.

3. Results and Discussion

All values are reported as ratios of the intensity in the secondary ion spectrum of the element of interest to ^{12}C, to eliminate matrix effects due to variations in the coal matrix and surface geometry at different analysis sites.

a) Oxidation under water with $^{18}O_2$

SIMS analysis showed no measurable uptake of ^{18}O. This result is not unexpected because of the relatively low solubility of O_2 in water and the slow establishment of equilibrium between gaseous and dissolved oxygen. It is possible that water does play a role in the reaction of O_2 with coal but this may only be evident if O_2 saturated with H_2O vapor is used. It would appear that the presence of liquid water inhibits oxidation by providing a barrier between the coal surface and O_2 gas.

b) Oxidation under $^{18}O_2$

i) Set 1. P804 and P832 in $^{18}O_2$ at 70°C and 104°C.

The most striking feature of these results, tables 1 and 2, is the wide variation between $^{18}O/C$ ratios at different spots on the coal surface. Consequently when the Arrhenius equation is used to calculate activation energies for coal P804 very different values are obtained using average $^{18}O/C$ ratios and those obtained from individual spots. Table 2 shows both average values, those obtained by using the lowest $^{18}O/C$ ratio at 70°C with the lowest ratio at 104°C, and the two highest ratios. It is worth noting that in this set insufficient oxidation occurred in coal P832 at 70°C to calculate an activation energy. When the experiment was repeated (Set 2) sufficient ^{18}O was found to calculate an activation energy. The difference in the results is due to the variability of oxidation at different sites on the coal.

ii) Set 2. The P804 and P832 coals were heated in 0.2 atm $^{18}O_2$ at 72°C and 104°C for 5 days, then subjected to SIMS analysis.

TABLE 1

Coal	Temp.	Spot	$^{18}O/C$	$^{18}O/C$ Avg.	Std. Dev.
P804	70°C	1	7.80×10^{-5}	6.0×10^{-4}	5.4×10^{-4}
		2	5.46×10^{-5}		
		3	1.27×10^{-3}		
		4	1.00×10^{-3}		
P804	104°C	1	4.30×10^{-4}	7.1×10^{-4}	5.4×10^{-4}
		2	0		
		3	1.60×10^{-3}		
		4	9.40×10^{-4}		
		5	5.8×10^{-4}		
P832	70°C	1	0	0	0
		2	0		
		3	0		
P832	104°C	1	7.00×10^{-3}	1.6×10^{-2}	2.2×10^{-2}
		2	1.23×10^{-3}		
		3	2.90×10^{-3}		
		4	5.40×10^{-2}		

TABLE 1 ^{18}O uptake over four days showing both individual spot analysis and average values.

TABLE 2

Values $^{18}O/C$ Used	Activation Energy
Average	53.8 kJ mol^{-1}
Lowest	75.6 kJ mol^{-1}
Highest	7.3 kJ mol^{-1}

Activation energies for coal P804 using average, highest and lowest $^{18}O/C$ ratios obtained at 70 and 104 °C.

TABLE 3

Coal	Temperature	$^{18}O/C^{*}$
KG15	72°C	9.26×10^{-2}
KG15	104°C	3.02×10^{-1}
P804	72°C	4.69×10^{-3}
P804	104°C	5.70×10^{-3}
P832	72°C	4.43×10^{-3}
P832	104°C	4.33×10^{-2}

TABLE 3: Set 2 for ^{18}O uptake over 5 days.

*These represent average values obtained from individual readings at 3 or 4 different spots on the coal surface.

TABLE 4

Coal	Activation Energy
KG15	39.9 kJ mol^{-1}
P804	6.5 kJ mol^{-1}
P832	77.0 kJ mol^{-1}

Activation energies obtained from $^{18}O/C$ ratios in Table 3.

The results from Sets 1 and 2 show clearly that while the activation energies obtained from several sites on the coal surface are useful in comparing different coals, much more information concerning oxidation of a given coal, and subsequently possible oxidation mechanisms, is available if individual reaction and sites are compared. Since it is difficult to examine equivalent sites on an individual coal oxidized at different temperatures a comparison was made between the reactivity of individual spots on the same coal at one temperature. Since indwelling mineral matter is suspected of having catalytic activity for oxidation the ratio of $^{18}O/Si$ was plotted against the $^{18}O/C$ ratio at different sites. The results are shown for P804, P832 and KG15 at several sites after oxidation at 104°C for five days in figures 1, 2 and 3 respectively. These results show a strong correlation between ^{18}O uptake and the presence of aluminosilicate minerals. This implies, as we and others have reported[11,20] that mineral matter is a good catalyst for coal oxidation. In addition table 2 shows clearly that the activation energy for regions of high oxygen uptake is much lower than regions of low uptake (7.3 vs 75.6 kJ mol^{-1}). This result is also consistent with the observed influence of the mineral matter.

Conclusions from $^{18}O_2$ Oxidation

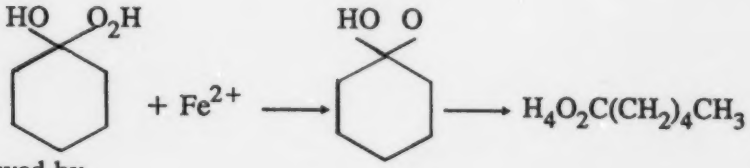
Taken together these results show that activation energies for oxidation measured by SIMS are useful for comparison of the surface reactivities of different coals. The comparison of the reactivities at different but equivalent sites is however far more accurate and SIMS measurements of oxidation within individual macerals and/or adjacent to different mineral inclusions provide valuable data. In fact this study shows significant reduction in the activation energies for oxidation in regions of high Si concentration. This result is indicative of the catalytic role of aluminosilicates in coal oxidation.

Chapter 4

OsO_4 STUDIES

1. Introduction

We have used a wide range of site-specific reagents to monitor the progress of surface oxidation in coal using both SIMS and XPS to follow surface reactivity[4,10,11]. This work has consistently supported a mechanism by which O_2 is adsorbed on the coal surface prior to the initiation of a free-radical chain oxidation. We have suggested, as have Lynch et al.[12], that surface peroxides are also important in the reaction. Peroxides can be used to introduce double bonds to organic molecules if the peroxide is treated with Fe^{2+} followed by Cu^{2+} solution[13]. Three reaction routes are possible:



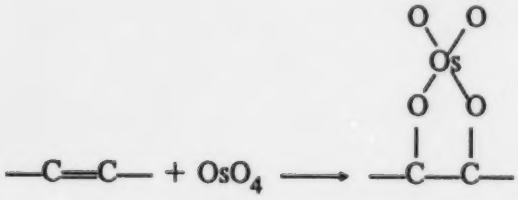
followed by

Route a) $2\ HO_2C(CH_2)_4CH_3\cdot \longrightarrow HO_2C(CH_2)_{10}CO_2H$

b) $HO_2C(CH_2)_4CH_3\cdot + CuCl_2 \longrightarrow HO_2C(CH_2)_4CH_2Cl + CuCl$

c) $HO_2C(CH_2)_4CH_3\cdot + CuSO_4 \longrightarrow HO_2C(CH_2)_3CH = CH_2 + Cu^+ + H^+$

Double bonds, introduced in this way would be expected to react readily with OsO_4 vapor to produce an OsO_4 adduct across the double bond[14].



Accordingly, in this section, we treat coal surfaces with Fe^{2+} and Cu^{2+} followed by exposure to OsO_4 vapor. The resulting surfaces were analyzed with SIMS, SEM and XPS to determine the presence of OsO_4, its surface distribution and oxidation state.

2. Experimental

The coals used were prepared as before, as were samples of polyethylene and polyisoprene. A sample of teflon sheet was obtained and was exposed to OsO_4 vapor without further treatment. All SIMS analyses were carried out using an O^- primary beam, 100 nA at 7.5 keV net energy. Images were collected from a spot 250 μm in diameter. Prior to imaging the coal samples were treated as follows:

a) Coal P832 was soaked in a 1:1 solution of 0.01 M $FeSo_4$/0.01 M $CuCl_2$ for 24 hours, rinsed with conductivity water for one hour, then exposed to 1 x 10^{-3} M RbOH for 10 minutes. The sample was finally washed and dried at 105°C for 24 hours followed by SIMS analysis.

Samples of P804 and KG15 were treated in a similar fashion.

b) Samples of P804, P832 and KG15 were exposed to 1:1 solutions of 0.02 M $FeSO_4$/0.02 M $CuSO_4$ for two hours, washed with conductivity water and air dried. The samples were then exposed to OsO_4 vapor above a 1% aqueous solution of OsO_4 in a sealed vessel for 24 hours. The samples were then air dried and were subjected to XPS analysis followed by SIMS. Additional samples were washed with 10^{-3} M HCl for four hours and were subjected both to SEM/EDX and XPS analysis.

c) Samples of teflon, polyisoprene, polyethylene and untreated coal were exposed to the OsO_4 vapor above a 1% aqueous solution of OsO_4 for 12 hours.

3. Results and Discussion

a) The SIMS images obtained following treatment of coal surfaces with $FeSO_4$/$CuCl_2$ followed by RbOH are similar in all cases. A typical result is shown in figure 4. This shows that Rb, Cu, Al and O have essentially co-incident SIMS images, a second area on the same coal in figure 5 shows that Cu and Cl images match. These results are consistent with reaction of $CuCl_2$ with free radicals generated from surface peroxides by reaction with Fe^{2+}. The Rb image shows surface organic acids while the Cu image is either CuCl, CuO or Cu_2O deposited in regions where organic Cl is present. The Al is indicative of catalytic activity by aluminosilicates.

This interpretation of the results, while not unique (Rb may be ion-exchanged with clays, and CuCl or $CuCl_2$ may be adsorbed), is consistent with the proposed oxidation mechanism.

b) Results for all coals were similar figures 6, 7 and 8 are typical and show substantial reaction with OsO_4 which is enhanced in aluminosilicate regions. In figure 7 two Os isotopes are shown. This result confirms the presence of Os on the coal surface rather than organic molecular secondary ions. XPS results, figure 9, show broad peaks for Os at 55.5 and 58.3 eV consistent with the OsO_4 adduct to double bonds on the coal surface. This result would be expected with double bond formation due to surface peroxides. Figure 10 the SEM/EDX shows that Os is still present on the surface after washing with HCl which would be expected to remove any OsO_2[14] formed as a result of oxidation of the coal surface by OsO_4. Figure 11 shows the XPS Os signal after washing with HCl. Two different Os species are now evident. The peaks at 55.5 and 58.3 are believed to be the OsO_4 adduct while the second set at 52.6 and 55.5 may be products of OsO_4 reduction by HCl[15]. These results fully support the presence of surface peroxides on coal during oxidation[16]. However the problem of the appearance of other Os species is puzzling.

c) Untreated Samples + OsO_4

Teflon showed no Os on its surface as a result of treatment, either in SIMS or XPS spectra. This result shows that deposition of Os on surfaces as OsO_4 or OsO_2 from the vapor phase does not occur in this system. Figure 12 shows the presence of unique XPS spectra of Os on untreated coal surfaces. This result is not consistent with the insertion of double bonds into the coal structure by reaction with Fe^{2+}/Cu^{2+} solutions. As well there is a good chance that OsO_4 may act as an oxidizing agent on coal surfaces. The XPS spectrum of Os on the surfaces shows peaks at 53.0, 55.0, 55.8 and 58.2. These results are consistent with surface oxidation of coal by OsO_4 but not with formation of OsO_4 adducts to double bonds.

Accordingly the XPS spectrum of Os was obtained from fresh polyisoprene surfaces exposed to OsO_4 vapor. The result, figure 13 shows peaks at 55.7 and 58.4. These are taken to represent the binding energy of OsO_4 in the double bond

adduct.

The polyethylene treated with OsO_4 yields peaks at 55.6, 57.8, 53.0 and 54.5, Figure 14. These are similar to the untreated coal results and are probably the result of reduction of OsO_4 in the polymer surface.

OsO_4 is widely used for tissue staining and a variety of oxidation states are found by XPS after the staining process. White et al.[17] identify the 55.2/52.4 eV doublet with Os(IV). Behrman[17,18] has pointed out that interpretation of Os 4f signals from XPS data is difficult because the binding energies of the oxidation states are very close and are strongly influenced by ligands. It is reasonable to conclude that the 4f Os doublet observed in polyisoprene at 58.3/55.7 is due to the OsO_4 adduct and that the inferences we have drawn from the SIMS images of coal are essentially correct. However the interpretation of the SIMS images is not unambiguous and since OsO_4 is a strong oxidizing agent Os oxidation states other the Os(VIII) are probably present on the coal surface. Accordingly while OsO_4 is indicative of reactive regions on the coal identification of Os with the OsO_4 double bond adduct cannot be made with certainty.

These results are summarized in Table 5.

Table 5

Sample	XPS Peak Energies/eV Os $4f_{5/2, 7/2}$	
Teflon	——	——
Polyisoprene	55.7/58.3	
Polyethylene	55.6/57.8	53.0/54.5
Coal (P832) Exposed to OsO_4 Vapor (After Treatment with Fe^{2+}/Cu^{2+})	55.5/58.3	
Coal (P832) Exposed to OsO_4 Vapor (After Treatment with Fe^{2+}/Cu^{2+}) Washed with 1M HCl	54.8/57.6	52.6/55.4
Coal (P832) Exposed to OsO_4 Vapor only	56.2/58.2	53.0/55.0

Conclusions

Reaction of coal with OsO_4 vapor followed by SIMS imaging is indicative of reactive sites on the coal surface. These sites are especially prone to reaction with OsO_4. In the case of coal treated with Fe^{2+}/Cu^{2+} to induce double bonds at sites corresponding to surface peroxides an OsO_4 adduct to the double bond is a likely product. Unfortunately the reactivity of OsO_4 and its ready reaction with polyethylene show that it is too strong an oxidizing agent to yield one product when exposed to hydrocarbons. XPS data provides convincing evidence that some OsO_4 is present as an adduct to olefins but the peaks are clearly overlapped by other Os species. As a result no unambiguous interpretation of this data is possible. The catalytic role of aluminosilicates is evident.

Chapter 5

Coal $Fe^{3+}/Fe(CN)_6^{3-}$

1. Introduction

Salehi and Hamilton[19] have used iron salts to stain coal surfaces as an aid in optical and electron microscopy. The authors did not speculate on the chemistry involved in the staining process. We suggest that the development of blue colors on the coal surfaces following exposure to $Fe^{3+}/Fe(CN)_6^{3-}$ solutions result from oxidation of the coal surface by Fe^{3+} with the subsequent formation of a charge-transfer complex (prussian blue) between $Fe^{2+}/Fe(CN)_6^{3-}$. Since this complex absorbs strongly in the visible region the reaction can be followed by colorimetry of appropriate coal slurries. The kinetics of the Fe^{3+} reduction are a direct measure of the reactivity of individual coals and may provide a means of predicting coal quality in specific industrial usage.

2. Experimental

1. Fresh coal at 30°C.

   Five of the coals used were obtained from the Argonne Premium Coal Sample Program while an additional two coals, P851 and P832 were mid volatile bituminous coals from Western Canada, supplied by CANMET, Ottawa, Canada. Samples were 100 mesh.

   Coal slurries containing Fe^{3+} were maintained at 30°C and stirred with a magnetic stir bar for periods ranging from five to twenty minutes. The slurries were then filtered to remove all solid matter. The resulting solution was subjected to colorimetric analysis at 700 nm. Coal slurries were prepared in two different ways: a) 0.30 g of coal were added to a solution prepared by mixing 20 ml of 0.60 M $FeCl_3$ with 10 ml of 0.30 M K_3FeCN_6 - this method did not yield satisfactory results and was used only for one sample; b) 0.30 g of coal were added to 20 ml of 0.60 M $FeCl_3$. This slurry was filtered after reaction with the coal and 10 ml of 0.30 M $K_3Fe(CN)_6$, which served as an indicator of the Fe^{3+}/coal interaction, was added.

2. Effect of temperature on reaction rate.

   Blind Canyon coal was treated as in Step 1 at temperatures of 40, 50 and

60°C.

3. Effect of air oxidation on reaction rate.

Five of the Argonne coals were oxidized in air at 108°C for five days. The samples were then reacted with Fe^{3+} as before.

4. Demineralization.

The Argonne coals were demineralized by soaking overnight in concentrated HCl, the resulting material was washed and treated with Fe^{3+} followed by $Fe(CN)_6^{3-}$.

3. Results and Discussion

1. Fresh coal.

The coal P851 was used to test the two procedures used in preparing the coal slurries. Figure 15 shows the results obtained by procedure a) while Figure 16 shows the results from procedure b). The first procedure leads to little measurable reaction while the second yields a well defined increase in the concentration of Fe^{2+} with time. These results suggest that K^+, $Fe(CN)_6^{3-}$ and/or the $Fe^{2+}/Fe(CN)_6^{3-}$ complex are strongly adsorbed on the coal surface and prevent further reaction of Fe^{3+} with the coal surface. The $Fe^{2+}/Fe(CN)_6^{3-}$ seems to be the most likely since Salehi and Hamilton observed a blue stain on coal surfaces after rinsing and drying coal surfaces identical to those used in preparing the coal slurries in procedure a). Procedure b) was used throughout the remainder of this study.

Figures 17-21 show the increase with Fe^{2+} concentration with time as well as the reaction rate obtained from the slope of this plot. In the case of the North Dakota coal only the first two points were used since the graph shows an initial fast reaction followed by a plateau with little further reaction. Figure 22 shows a plot of reaction rate vs O/C ratio for each of the Argonne coals, Figure 23 shows the same kinetic data plotted against H/C for the coals.

It is clear that each coal yields a reaction rate which is strongly correlated with both O/C and H/C ratios. The North Dakota coal shows an initial fast reaction while the other coals have an apparent non-zero intercept for Fe^{2+} in the Fe^{2+} vs time plot. This result may be due to an initial rapid reaction or to Fe^{2+}

present in the coal prior to reaction.

Clearly Fe^{3+} in solution oxidizes coal surfaces and the resulting Fe^{2+}/Fe^{3+} charge transfer complex may be used as an indicator of the extent of reaction when Fe^{3+} is introduced as $Fe(CN)_6^{3-}$.

The $Fe^{2+}/Fe(CN)_6^{3-}$ is strongly adsorbed on the coal surface and inhibits further reaction. The kinetics of the Fe^{3+} reduction can be followed colorimetrically if $K_3Fe(CN)_6$ is added to solutions obtained from coal slurries in contact with $FeCl_3$.

The kinetics of Fe^{3+} reduction is correlated with the O/C and H/C ratios of the coal.

2. Temperature and reaction rate.

Figure 24 shows the reaction rate obtained at40, 50 and 60° from Blind Canyon coal. The rate shows a steady increase with temperature. The Arrhenius equation can be used to estimate the activation energy, these results are shown in table 6.

TABLE 6

Temperatures Used	Activation Energy
50/40	34.5 kJ mol^{-1}
60/50	13.8 kJ mol^{-1}
60/40	24.9 kJ mol^{-1}

This preliminary data is subject to considerable error but indicates that the activation energies are low as would be expected for a catalyzed reaction. In addition the activation energy appears to fall with increasing temperature. This

may be due to an increased rate of desorption of Fe^{2+} from the coal surface, removal of Fe^{2+} as a reaction product may speed reaction.

3. Oxidized coal.

Figures 25-29 show the results of mild oxidation on the kinetics of the $Fe^{3+}/Fe(CN)_6^{3-}$ reaction. There is little change, within experimental error with the exception of the North Dakota coal where the rate appears to be much reduced. This latter effect is almost certainly due to uncertainty in assigning the first data point in the kinetic data. We anticipate that improvements in the experimental system will lead to more satisfactory results.

4. Demineralized samples.

Only two demineralized samples were attempted, Stockton and Illinois #6. This work was undertaken to insure that indwelling iron in the coal matrix did not interfere with our results. Figures 30 and 31 show no significant effect on the reaction kinetics.

All results obtained at 30° are summarized in table 7.

TABLE 7

Coal	Rate fresh	Rate oxidized	Rate demineralized
P851	4.24×10^{-6}		
WYODAK	8.5×10^{-6}	4.8×10^{-6}	
POCAHONTAS	1.0×10^{-6}	1.5×10^{-6}	
STOCKTON	2.6×10^{-6}	2.1×10^{-6}	2.8×10^{-6}
NORTH DAKOTA	5.8×10^{-5}	3.3×10^{-6}	
ILLINOIS #6	6.9×10^{-6}	6.4×10^{-6}	8.1×10^{-6}

Conclusions

The results show that Fe^{3+} is readily reduced at the coal surface and that the rate of reduction of the iron, and hence the oxidation of the coal surface can be followed colorimetrically if $Fe(CN)_6^{3-}$ is present in the coal slurry leading to the formation of the blue charge-transfer complex $Fe^{2+}/Fe(CN)_6^{3-}$ (Prussian Blue). The detailed kinetics depend on the coal type and the O/C and H/C ratio.

In addition, the quinhydrone/hydroquinone couple seems to provide a good model for the type of coal surface undergoing oxidation since:

$$Fe^{3+} + e \longrightarrow Fe^{2+} \qquad E^\bullet = 0.77\ V$$

$$\text{while } C_6H(OH)_2 \longrightarrow C_6H_4O_2 + 2\,H^+ + e \qquad E^\bullet = 0.306 \text{ at pH } 7$$

indicating Fe^{3+} is capable of reducing this species.

Neither demineralization nor oxidation of the coal show any pronounced changes in Fe^{3+} reactivity suggesting that indwelling Fe does not contribute to the reaction and that air oxidation under mild conditions does not introduce oxygen functional groups capable of reducing Fe^{3+}.

Chapter 6

CONCLUSIONS

Taken together the results agree with those obtained in our previous work. Specifically that at low temperatures the oxidation of coal proceeds by a free-radical chain mechanism. In addition the generation of free radicals is catalyzed by mineral matter, generally present in the form of aluminosilicates. In this study we have also noted that, for SIMS analysis:

1. Measurements of the uptake of ^{18}O on coal surfaces oxidized in $^{18}O_2$ show that the extent of oxidation varies by as much as two orders of magnitude from one site 200 μ in diameter on the coal surface to another.

2. Activation energies for oxidation can be obtained from individual pairs of sites on coal surfaces oxidized at different temperatures.

3. Averages of oxidation uptake at a large number of individual sites may be used to compare the reactivities of different coals.

4. In a given coal oxidation activation energies obtained from sites having high yields of Si and/or Al in the secondary ion spectrum have substantially lower activation energies than those obtained from less mineralized regions.

The OsO_4 results are consistent with the presence of peroxides on the coal surface, however OsO_4 is a strong enough oxidizing agent to react with the coal resulting in deposition of significant Os on the coal. SIMS analysis shows well defined patterns of Os on coal surfaces exposed to OsO_4 gas. XPS yields Os 4f signals corresponding to those obtained from reaction of OsO_4 with polyisoprene and hence are indicative of OsO_4 addition to double bonds. Unfortunately it is clear that other Os species are present and the literature on Os XPS spectra cautions against assigning Os oxidation states based on XPS results because the spectra are densely packed and subject to considerable variation depending on surrounding ligands. We conclude that OsO_4 may be a useful chemical oxidant to study coal reactivity but that the results obtained cannot be used to varify the presence of oelfins generated from surface peroxides.

The $FeCl_3/K_3Fe(CN)_6$ system has proven to be of special interest. Our results show:

1. Development of intense blue colors on coal surfaces treated with $FeCl_3/K_3Fe(CN)_6$ solutions and in coal slurries of the same solution result from the formation of $Fe^{2+}/Fe^{3+}(CN)_6^{3-}$, Prussian Blue.
2. $Fe(CN)_6^{3-}$ adsorbs strongly on coal surfaces so that reaction in slurries is not evident after the initial reaction phase resulting in coverage of the coal surface with Prussian Blue is complete.
3. If coal is reacted with $FeCl_3$, $K_3Fe(CN)_6$ can be used as a colorimetric indicator of the extent of oxidation of the coal by Fe^{3+} yielding Fe^{2+} if the Fe^{2+} solution is removed from the slurry before addition of $K_3Fe(CN)_6$.
4. The E° values for oxidation of hydroquinone and reduction of Fe^{3+} suggest that reaction of the iron ion with coal occurs at quinone-like sites i.e. aromatic ketones or phenols. In consequence the kinetics of the $Fe^{3+} \longrightarrow Fe^{2+}$ reaction are indicative of the degree of oxidation of the coal.
5. It is possible to construct an instrument capable of following the iron reduction colorimetrically and to predict the thermal and coking properties of the coal from the observed reaction kinetics.
6. The most striking feature of the concentration of Fe^{2+} vs time plots is the non-zero intercept. This may be due to either:
   a) Initial fast reaction or
   b) Fe^{3+} and/or Fe^{2+} present in the coal.

   Since demineralization fails to remove this anomaly we conclude that reaction is more rapid in the interval between time zero and five minutes. We are improving the experimental technique to address this problem.
7. Air oxidation of the material prior to analysis did not significantly affect the rate of oxidation by Fe^{3+}. This is consistent with our hypothesis that hydroquinone-quinone type groups are involved if, as is likely, these functional groups are not formed by mild air oxidation.

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ACKNOWLEDGEMENTS

The author wishes to acknowledge the support and assistance received from Surface Science Western.

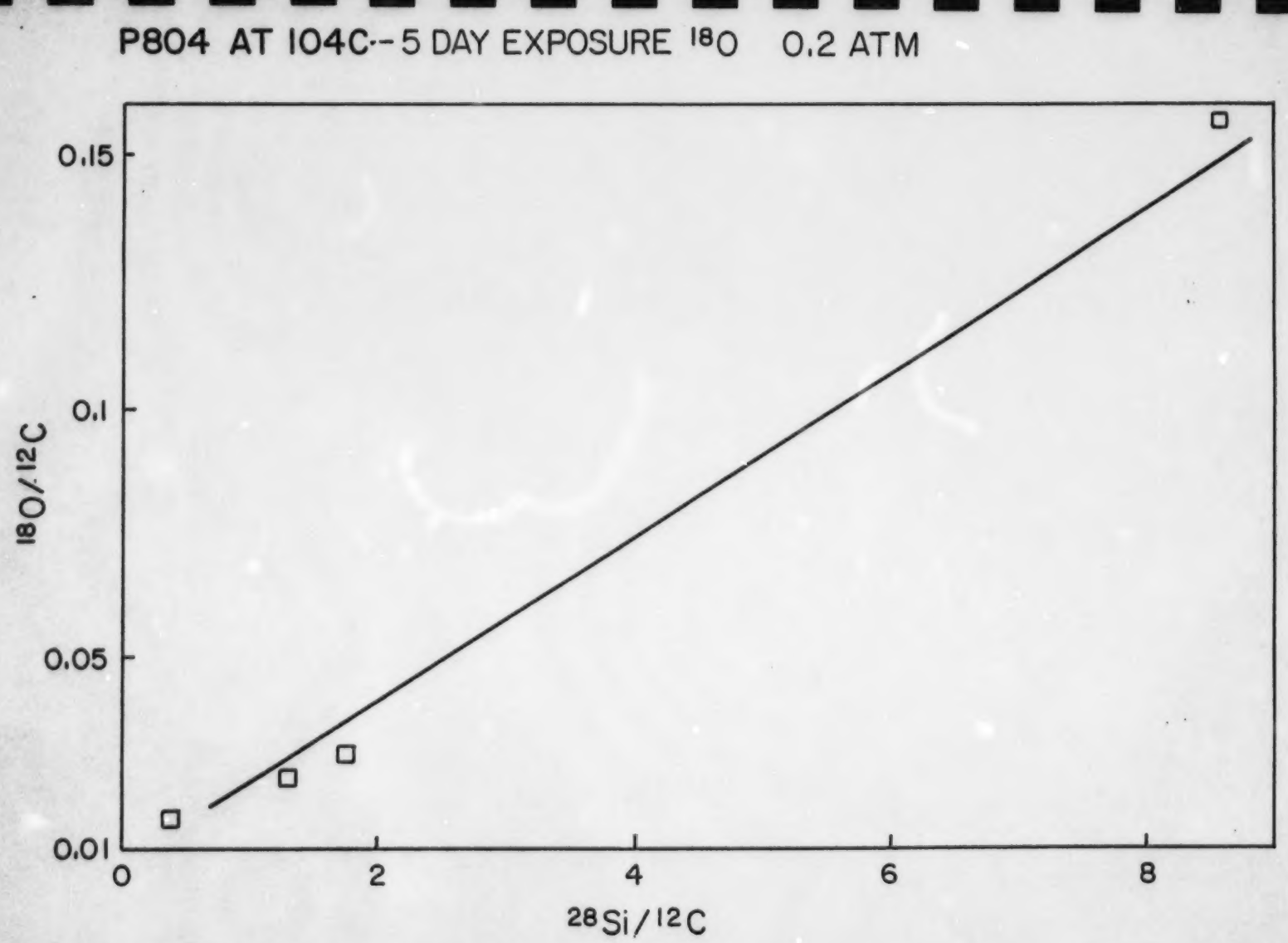
P804 AT 104C--5 DAY EXPOSURE ^{18}O 0.2 ATM
0.15
0.1
0.05
0.01
$^{18}O/^{12}C$
0
2
4
6
8
$^{28}Si/^{12}C$

Figure 1

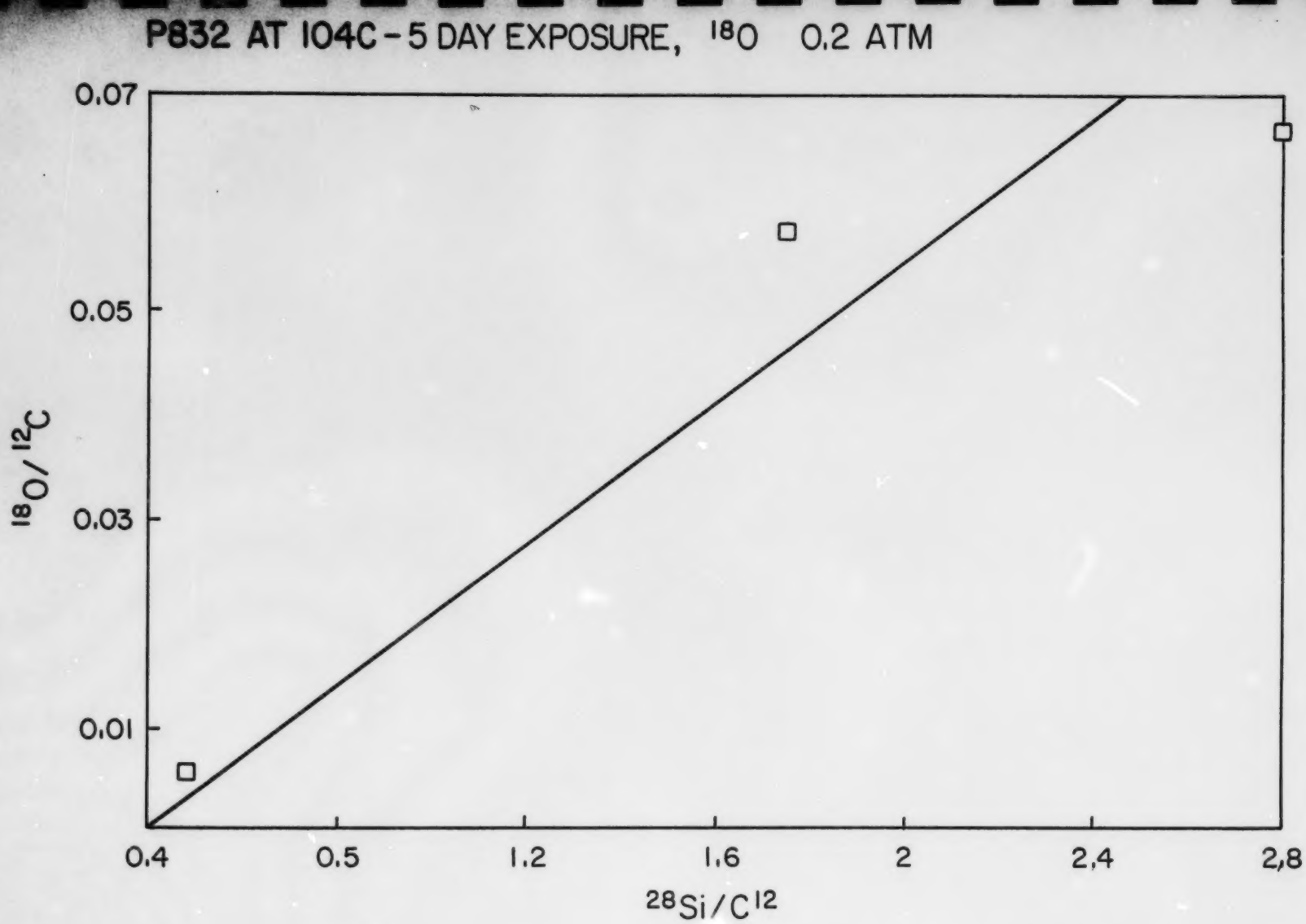
P832 AT 104C - 5 DAY EXPOSURE, ^{18}O 0.2 ATM
0.07
0.05
0.03
0.01
$^{18}O/^{12}C$
0.4
0.5
1.2
1.6
2
2.4
2.8
$^{28}Si/C^{12}$

Figure 2

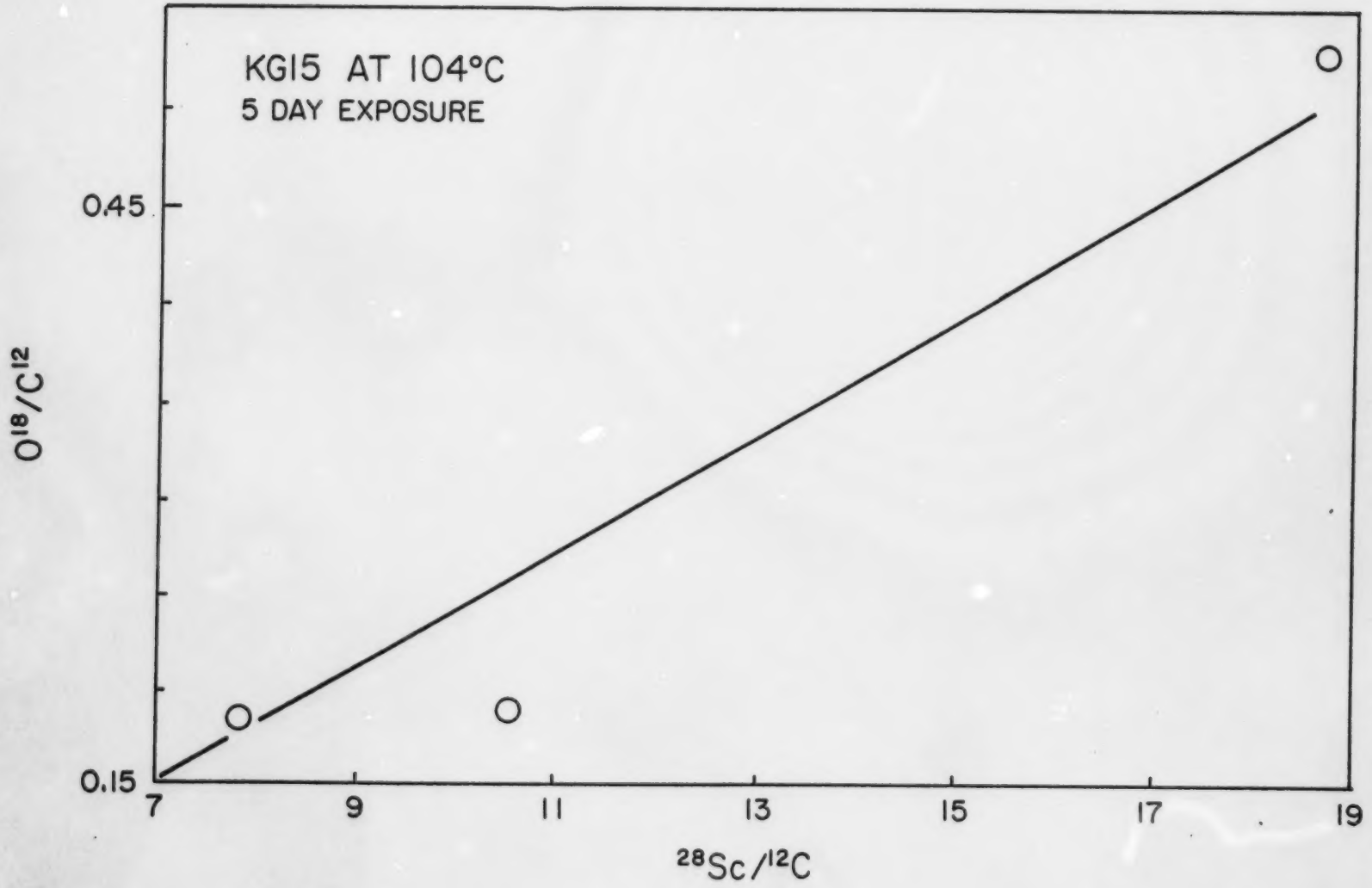
KG15 AT 104°C
5 DAY EXPOSURE
0.45
0.15
O18/C12
7
9
11
13
15
17
19
28Sc/12C

Figure 3

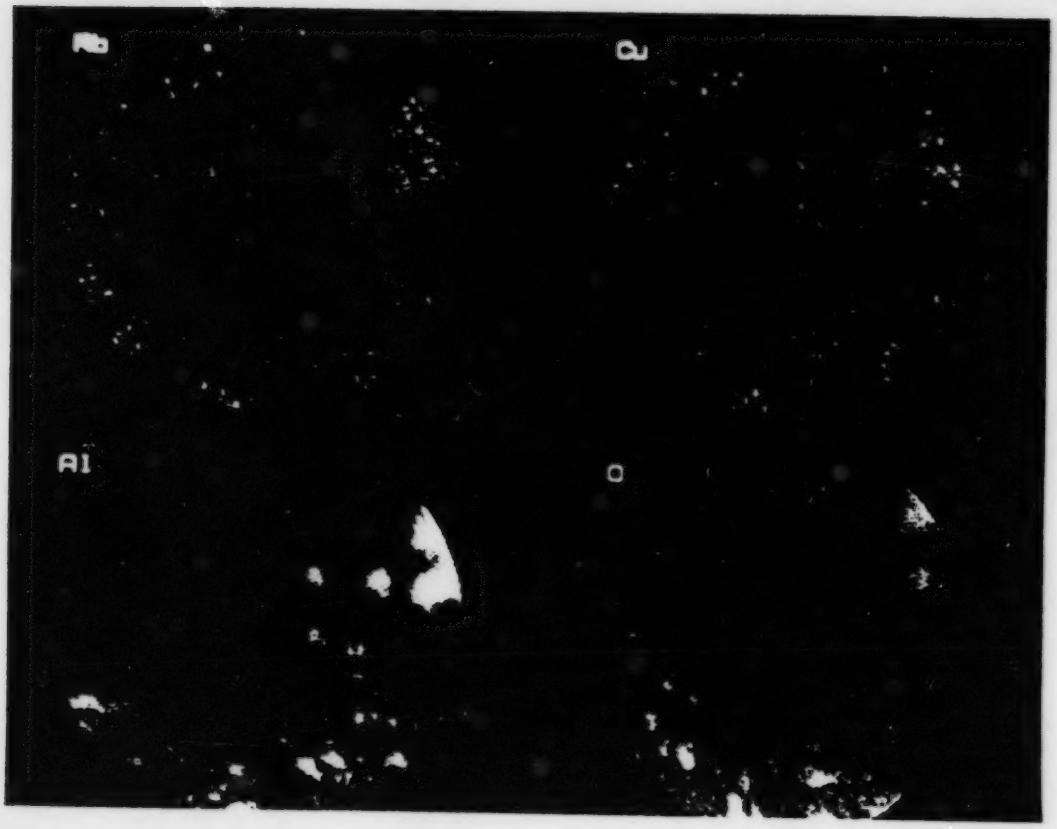

Figure 4. SIMS images for Rb, Cu, Al and O on coal following reaction with $FeSO_4/CuCl_2$ and RbOH.

Figure 5. SIMS images of Cu and Cl on a coal surface following reaction with $FeSO_4/CuCl_2$.

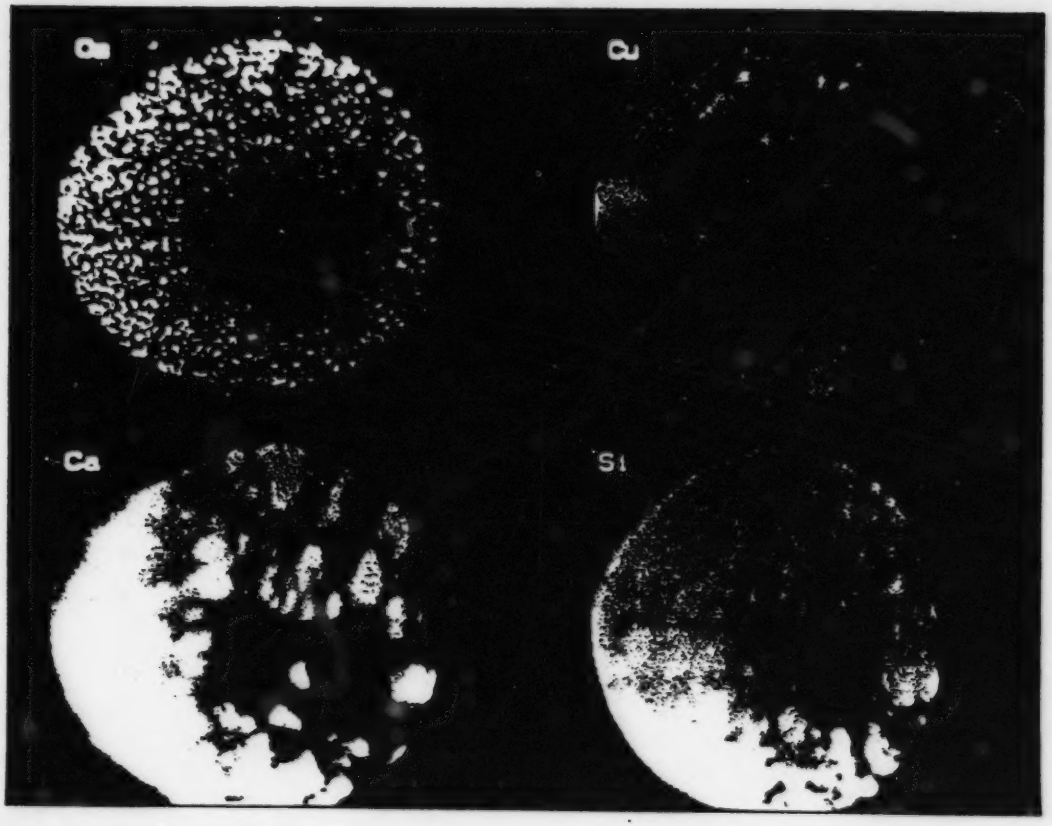

Figure 6. SIMS images of Os, Cu, Ca and Si from coal following reaction of the surface with $FeSO_4/CuSO_4$ followed by exposure to O_5O_4 vapor.

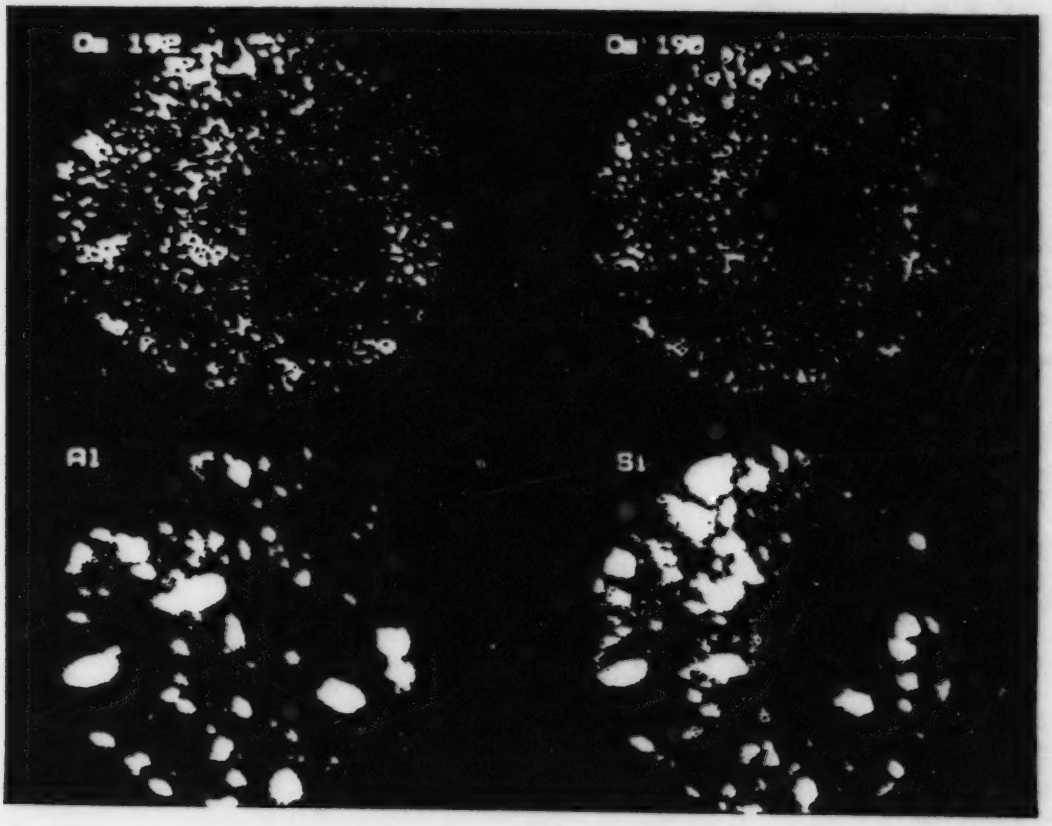

Figure 7. SIMS images of ^{192}Os, ^{190}Os, Al and Si on a coal surface reacted with $FeSO_4/CuSO_4$ followed by exposure to O_5O_4 vapor.

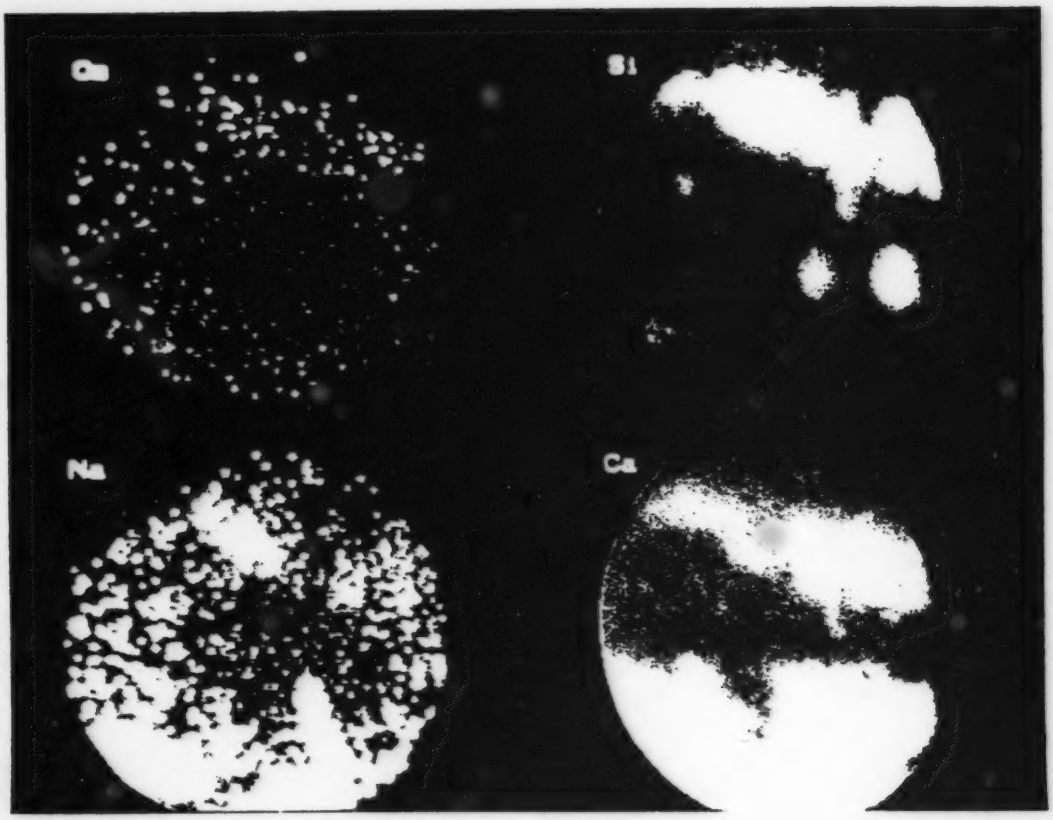

Figure 8. SIMS images of Os, Si, Na and Ca on a coal surface reacted with $FeSO_4/CuSO_4$ followed by exposure to O_5O_4 vapor.

Treated Coal with OsO_4

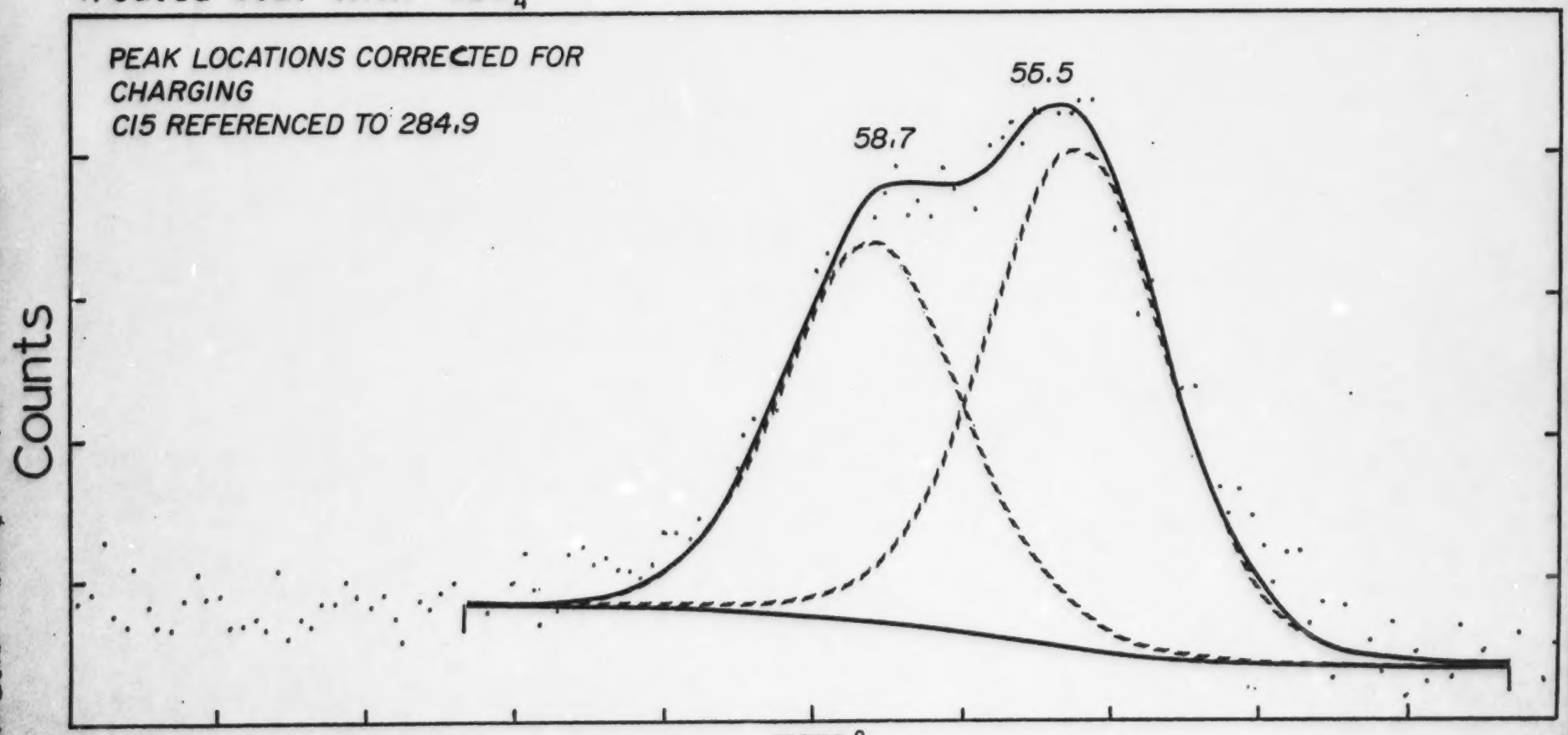

FIGURE 9

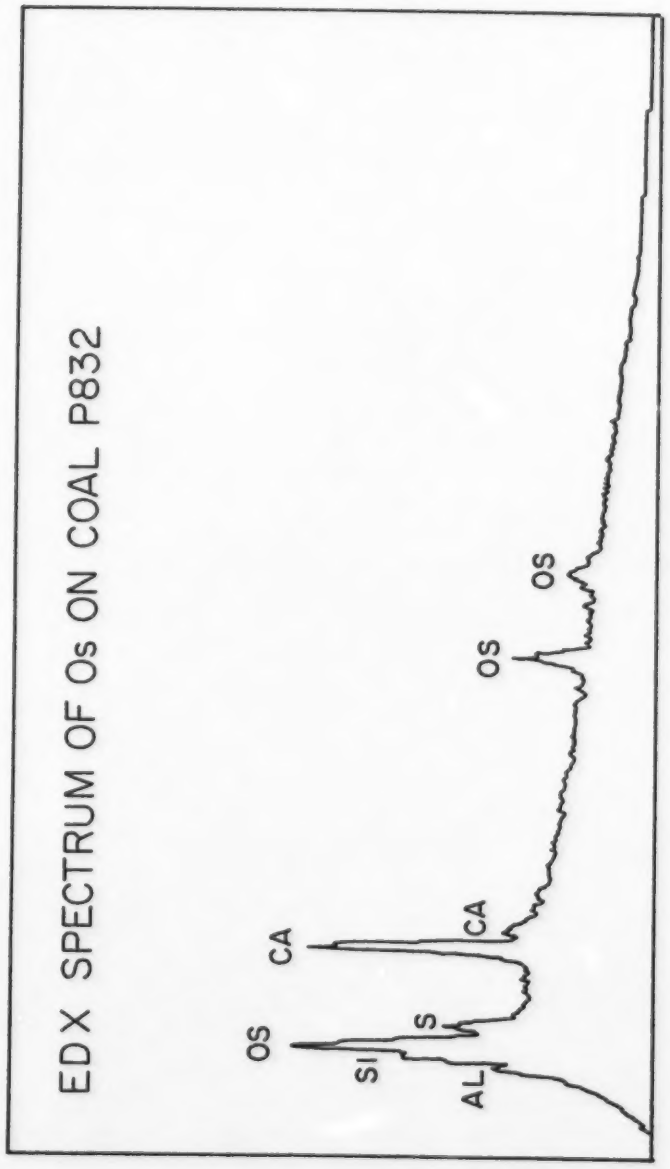

FIGURE 10

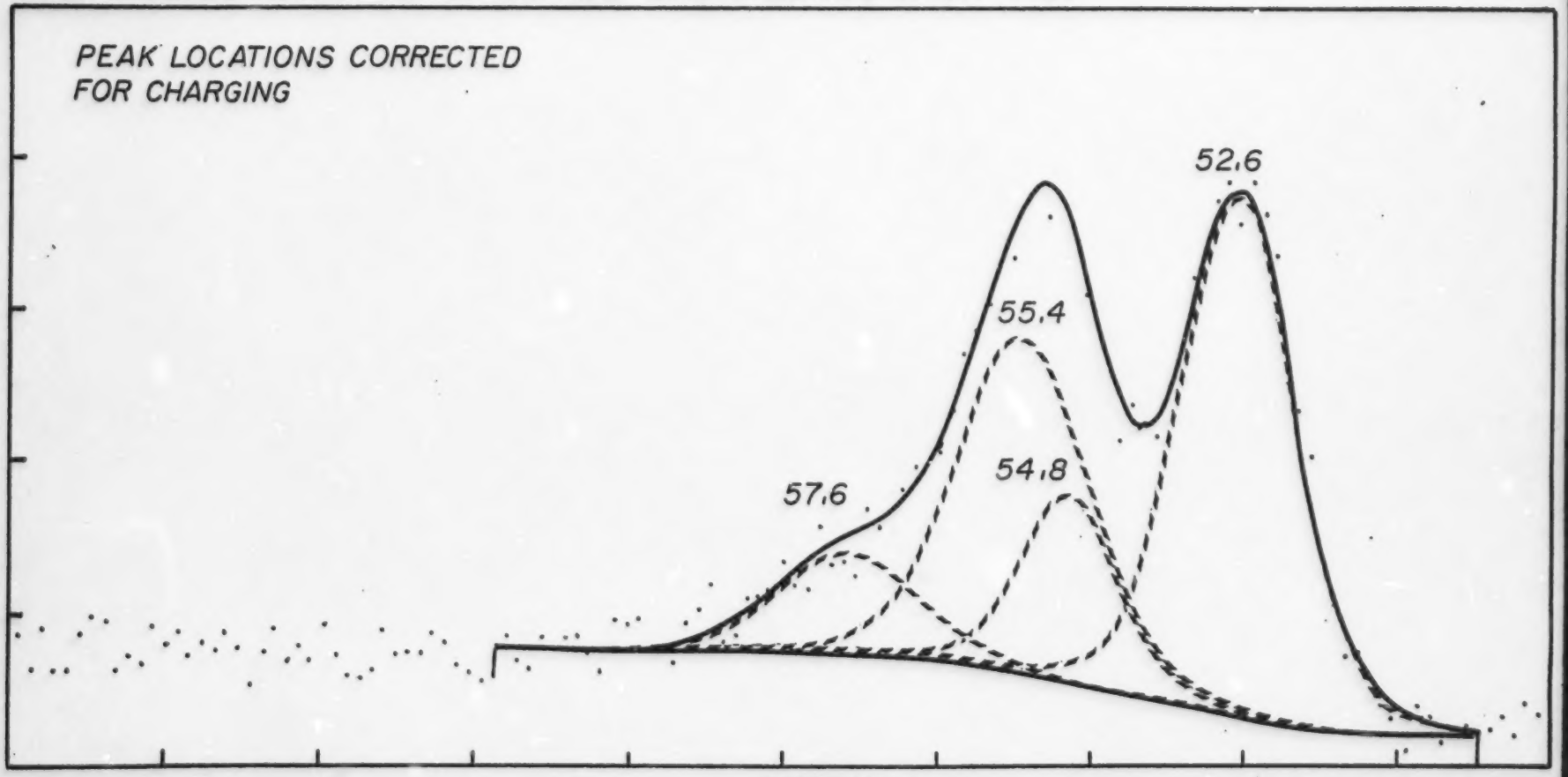
Coal treated with Os Tetraoxide and washed with HCl
PEAK LOCATIONS CORRECTED
FOR CHARGING
52.6
55.4
54.8
57.6
Counts
Binding Energy (eV)

FIGURE 11

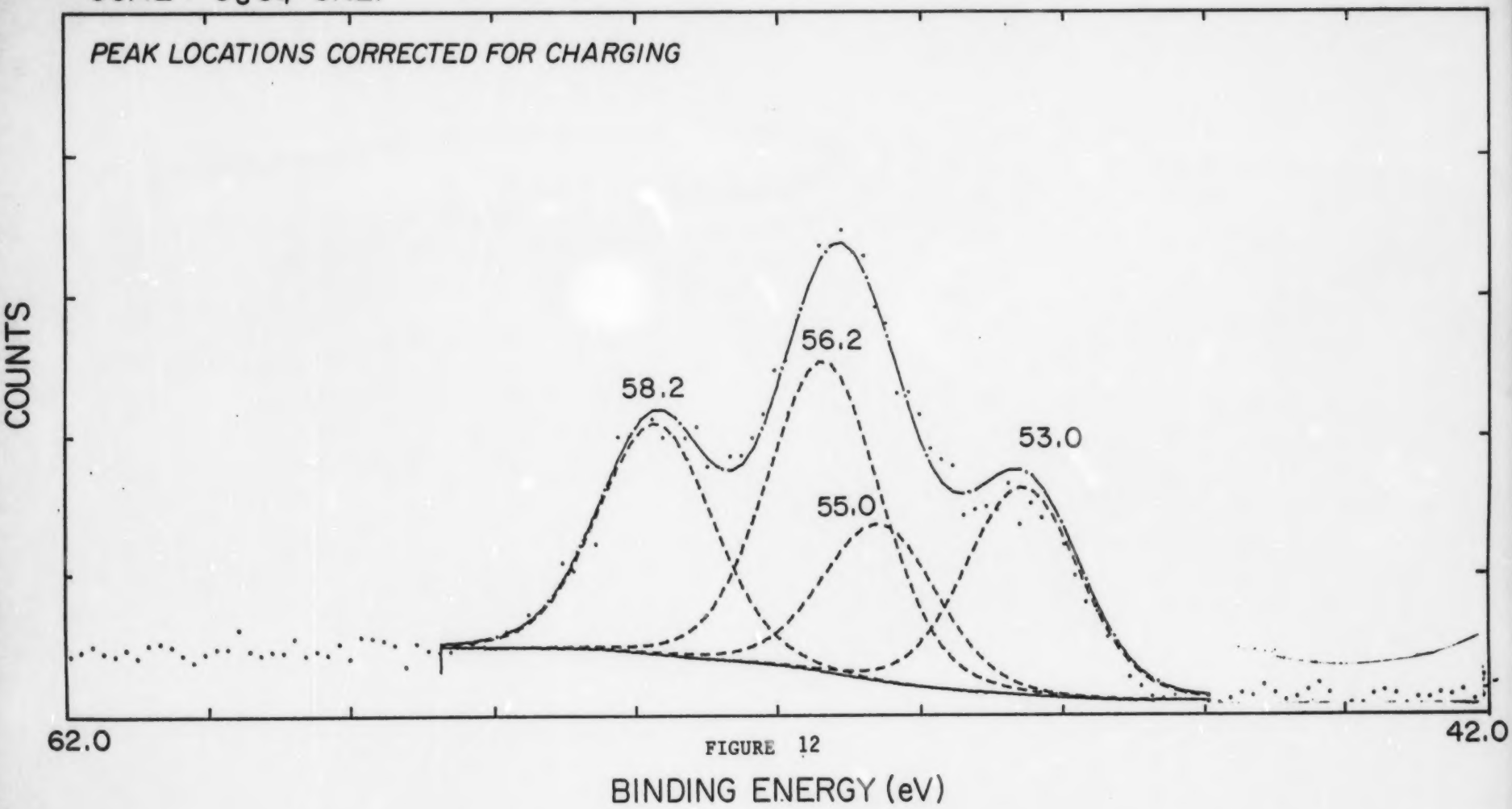
COAL + OsO_4 ONLY
PEAK LOCATIONS CORRECTED FOR CHARGING
COUNTS
58.2
56.2
55.0
53.0
62.0
42.0
BINDING ENERGY (eV)

FIGURE 12

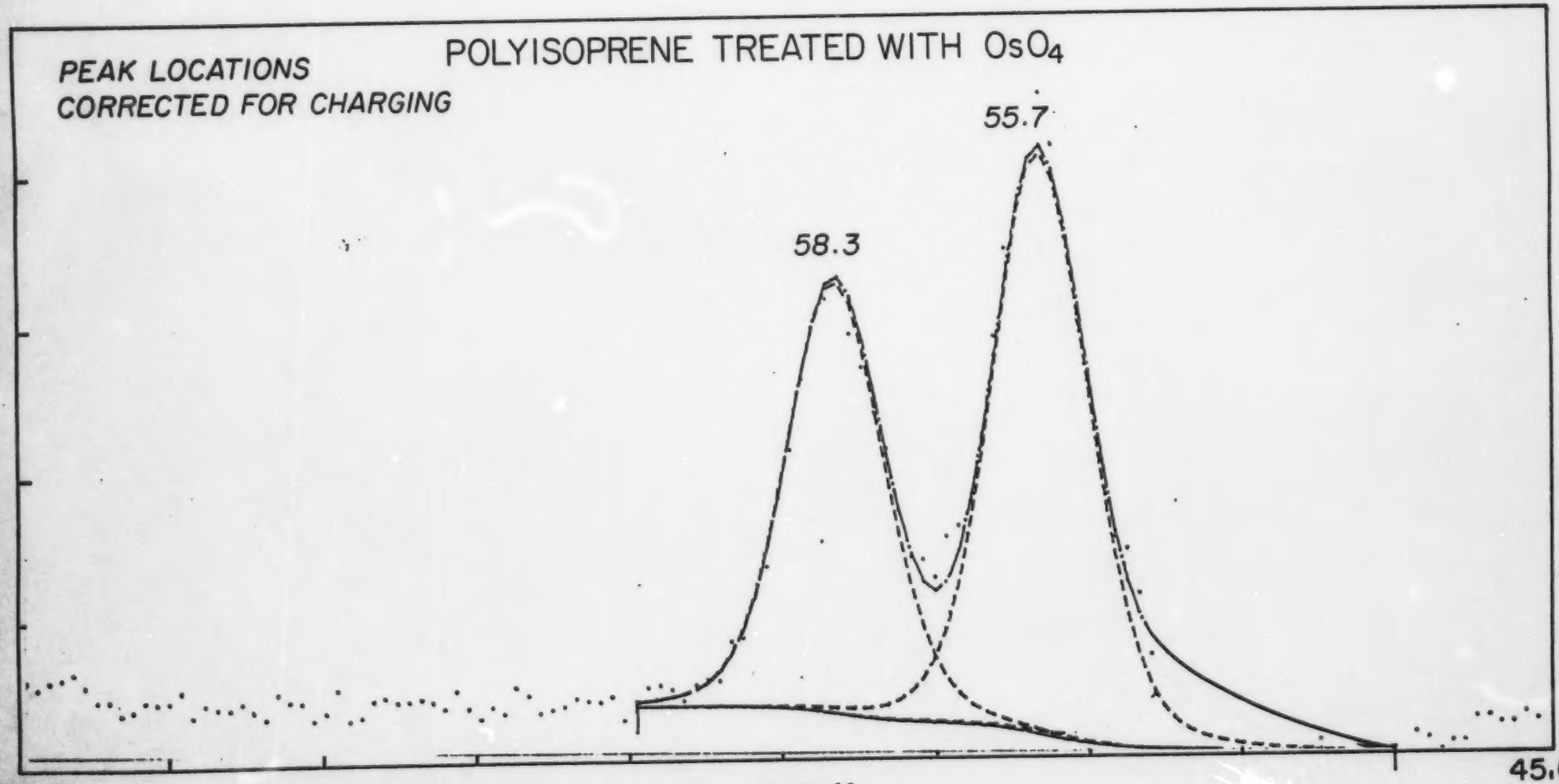
POLYISOPRENE TREATED WITH OsO_4
PEAK LOCATIONS
CORRECTED FOR CHARGING
55.7
58.3
65.0
45.0
BINDING ENERGY (eV)

FIGURE 13

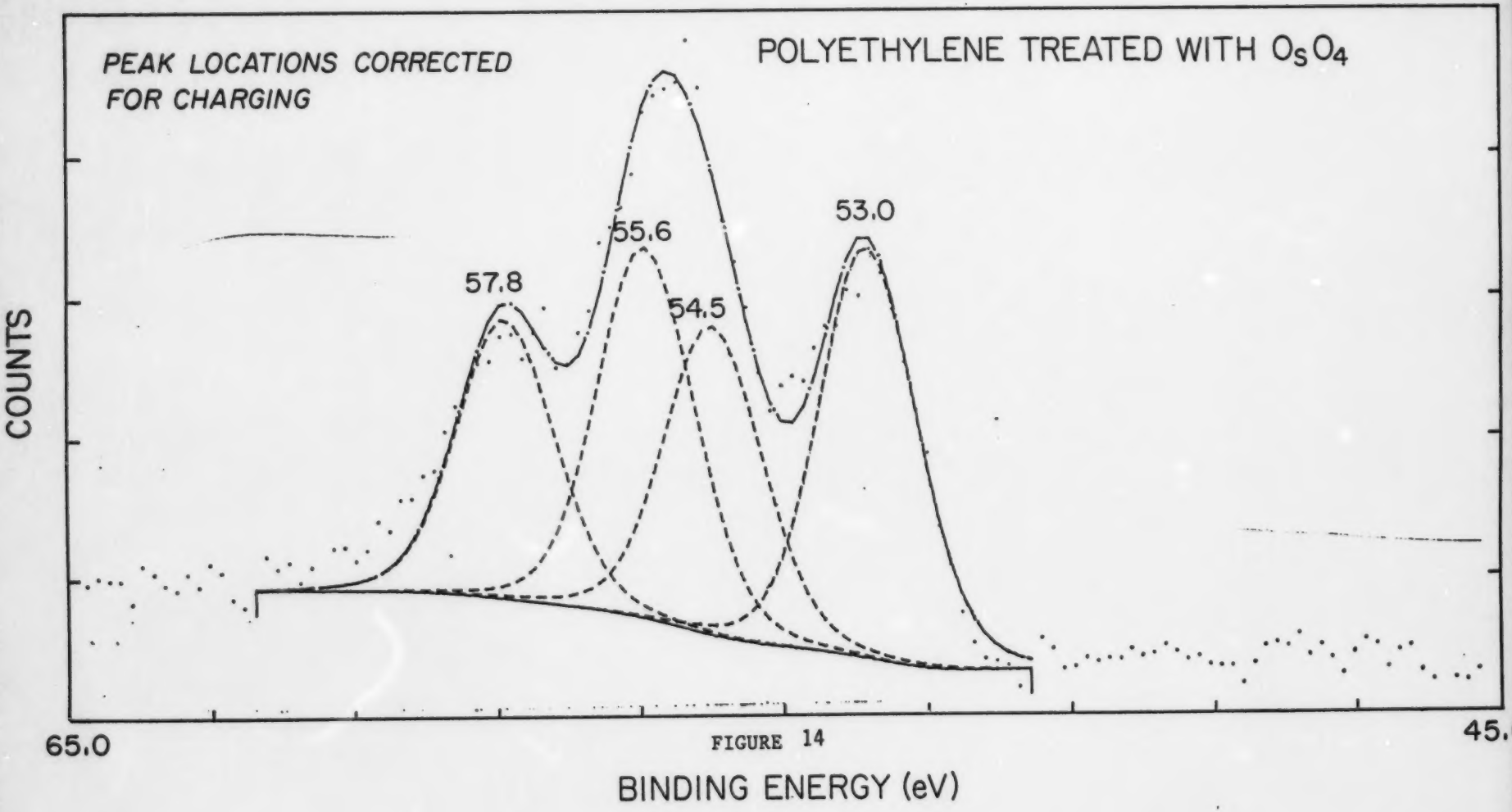
PEAK LOCATIONS CORRECTED
FOR CHARGING
POLYETHYLENE TREATED WITH O_sO_4
57.8
55.6
54.5
53.0
COUNTS
65.0
45.0
BINDING ENERGY (eV)

FIGURE 14

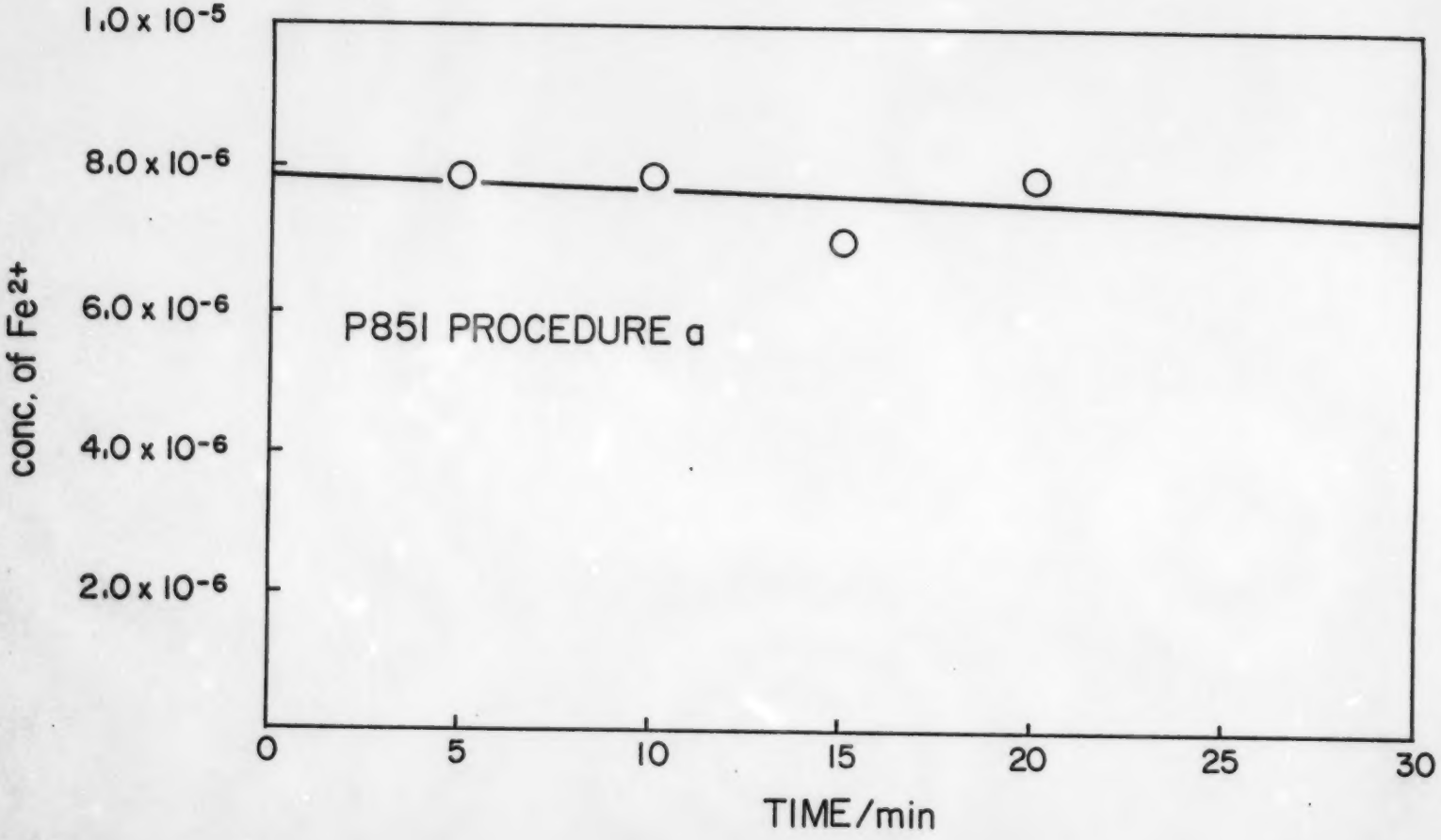
1.0 x 10-5
8.0 x 10-6
6.0 x 10-6
4.0 x 10-6
2.0 x 10-6
conc. of Fe2+
P851 PROCEDURE a
0
5
10
15
20
25
30
TIME/min

Figure 15

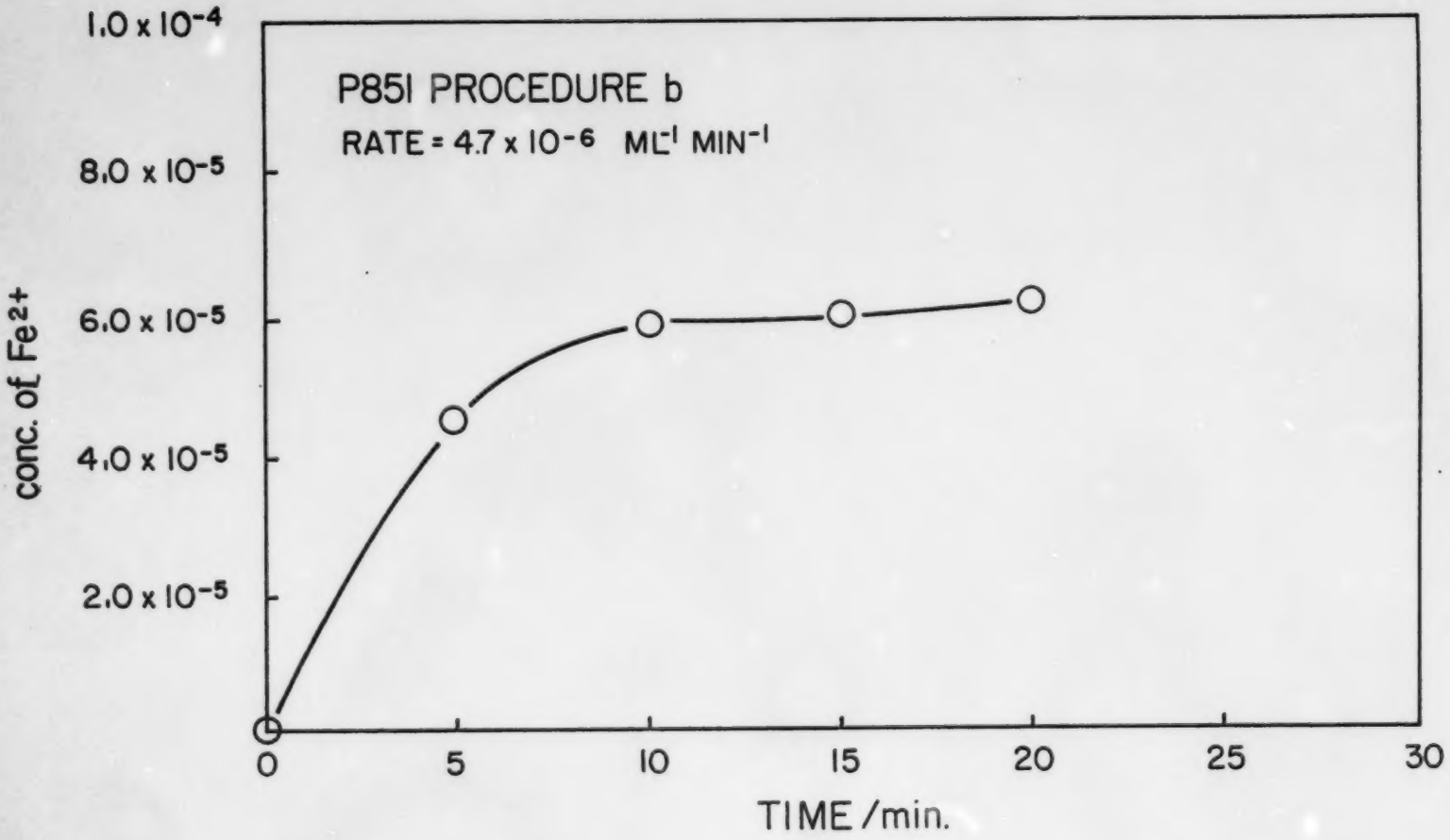
P851 PROCEDURE b
RATE = 4.7 x 10-6 ML-1 MIN-1
1.0 x 10-4
8.0 x 10-5
6.0 x 10-5
4.0 x 10-5
2.0 x 10-5
conc. of Fe2+
0
5
10
15
20
25
30
TIME /min.

Figure 16

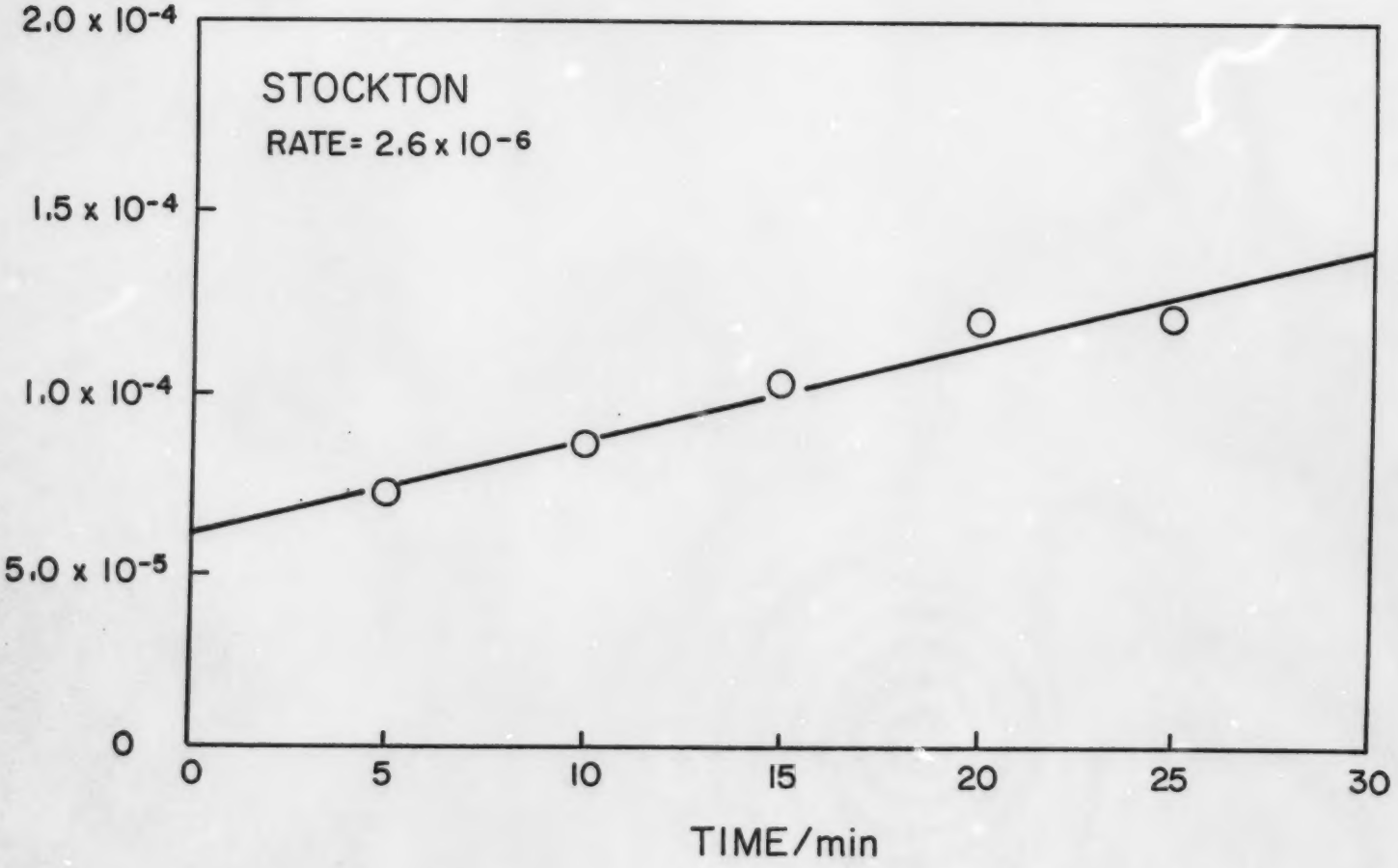
2.0 x 10-4
1.5 x 10-4
1.0 x 10-4
5.0 x 10-5
0
STOCKTON
RATE= 2.6 x 10-6
0
5
10
15
20
25
30
TIME/min

Figure 17

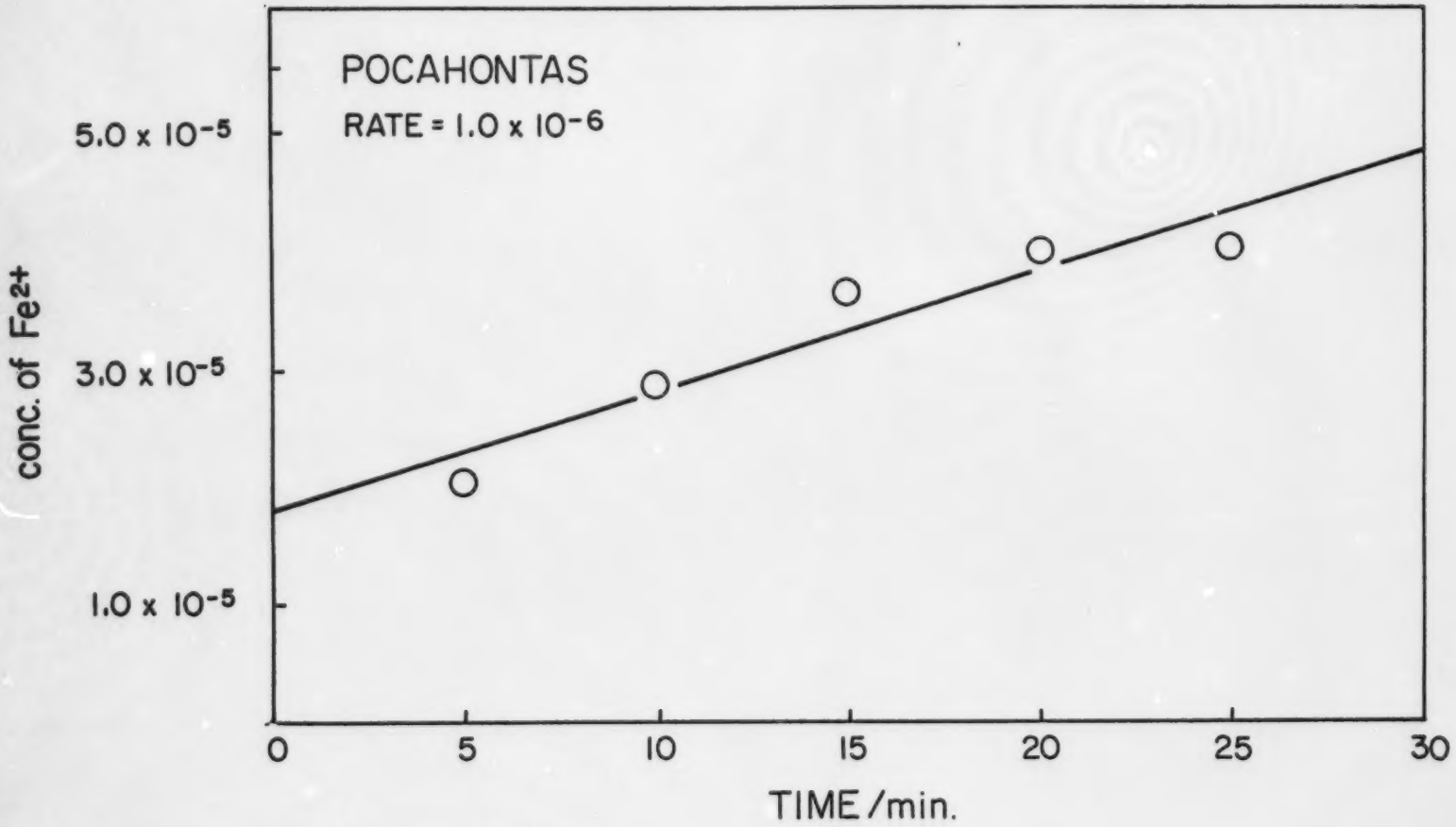
POCAHONTAS
RATE = 1.0 x 10-6
5.0 x 10-5
3.0 x 10-5
1.0 x 10-5
conc. of Fe2+
0
5
10
15
20
25
30
TIME/min.

Figure 18

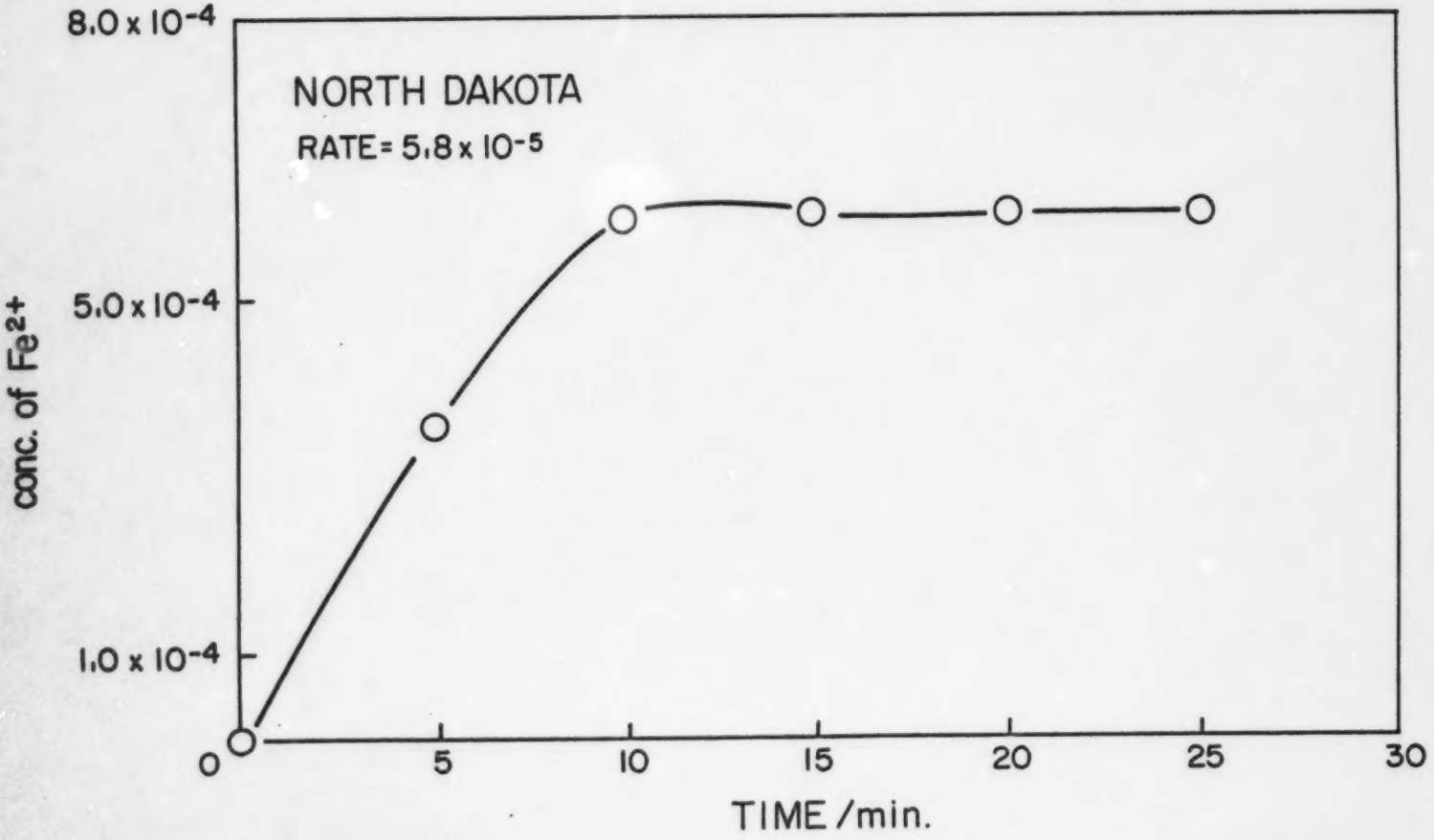
8.0 x 10-4
NORTH DAKOTA
RATE= 5.8 x 10-5
5.0 x 10-4
conc. of Fe2+
1.0 x 10-4
0
5
10
15
20
25
30
TIME /min.

Figure 19

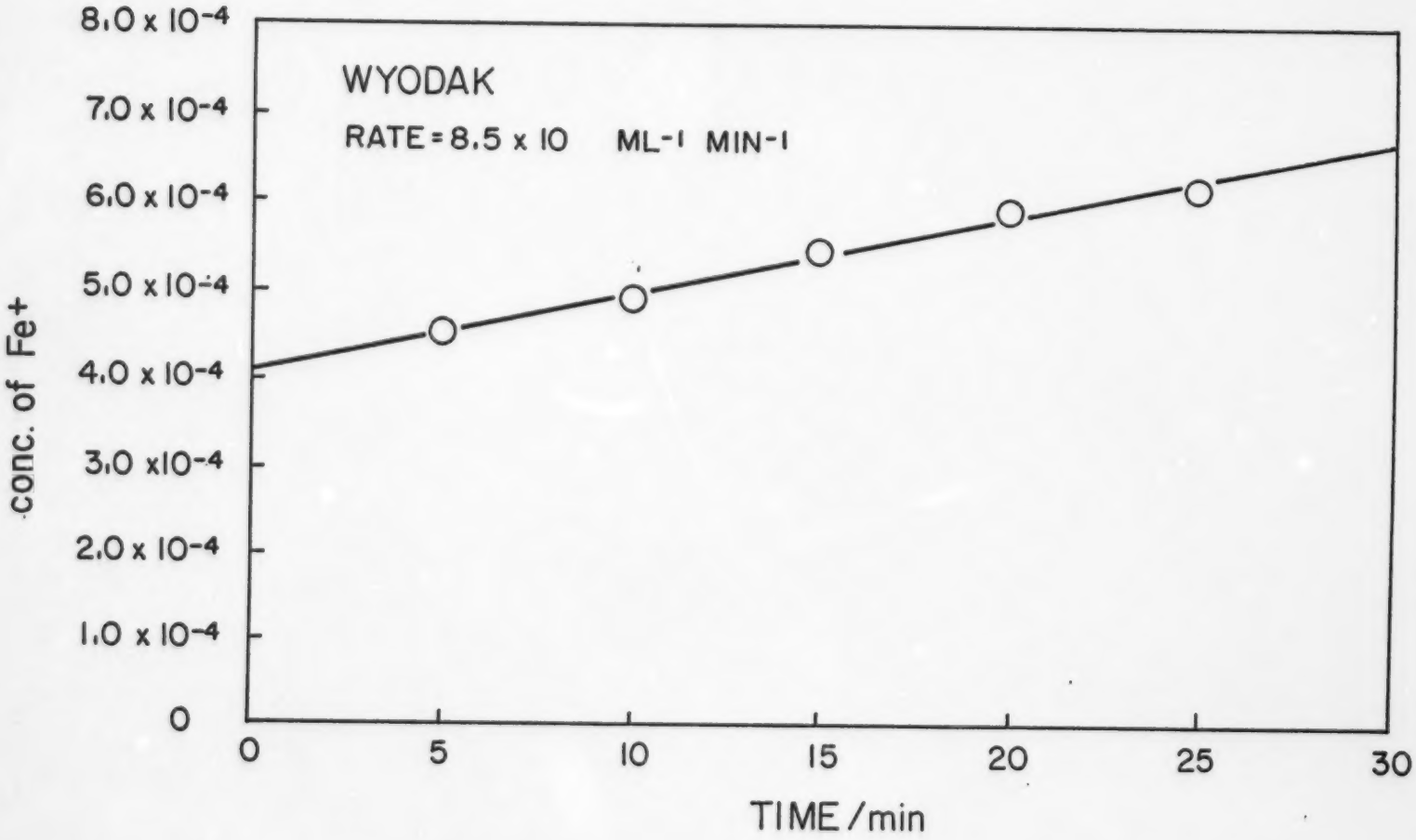
WYODAK
RATE = 8.5 x 10 ML-1 MIN-1
8.0 x 10-4
7.0 x 10-4
6.0 x 10-4
5.0 x 10-4
4.0 x 10-4
3.0 x10-4
2.0 x 10-4
1.0 x 10-4
0
conc. of Fe+
0
5
10
15
20
25
30
TIME /min

Figure 20

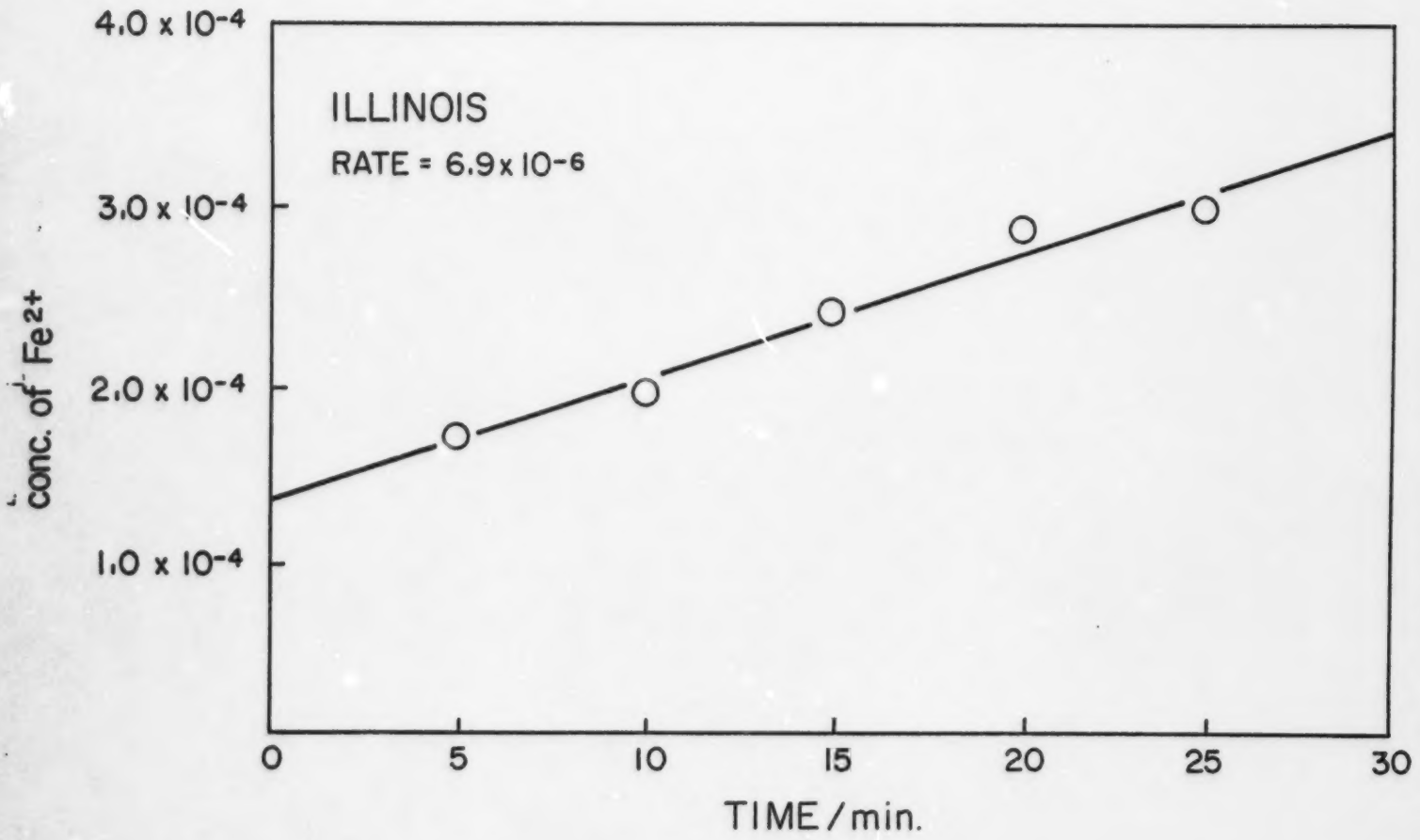
4.0 x 10-4
3.0 x 10-4
2.0 x 10-4
1.0 x 10-4
conc. of Fe2+
ILLINOIS
RATE = 6.9x 10-6
0
5
10
15
20
25
30
TIME / min.

Figure 21

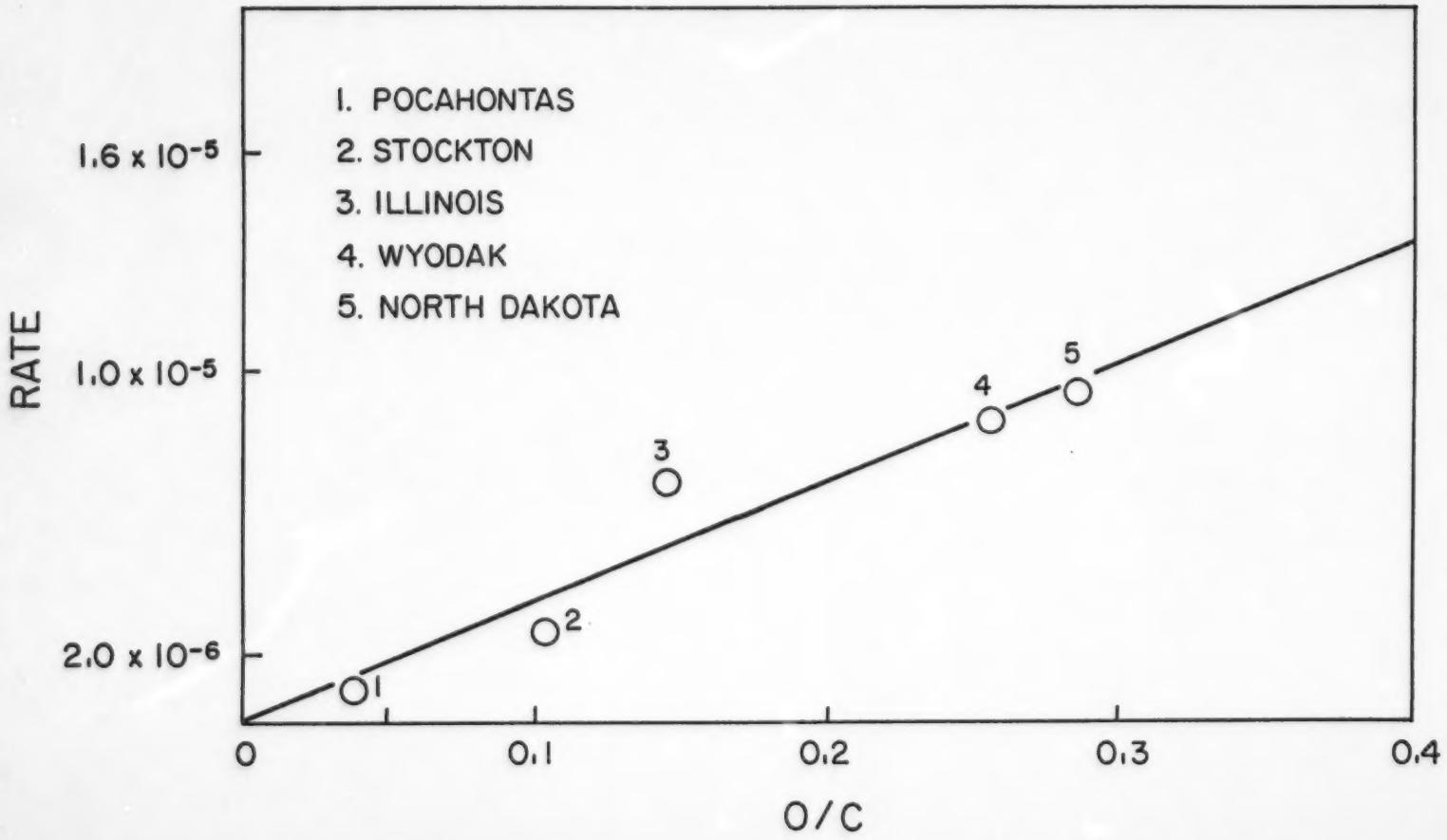
1. POCAHONTAS
2. STOCKTON
3. ILLINOIS
4. WYODAK
5. NORTH DAKOTA
RATE
1.6 x 10-5
1.0 x 10-5
2.0 x 10-6
0
0.1
0.2
0.3
0.4
O/C

Figure 22

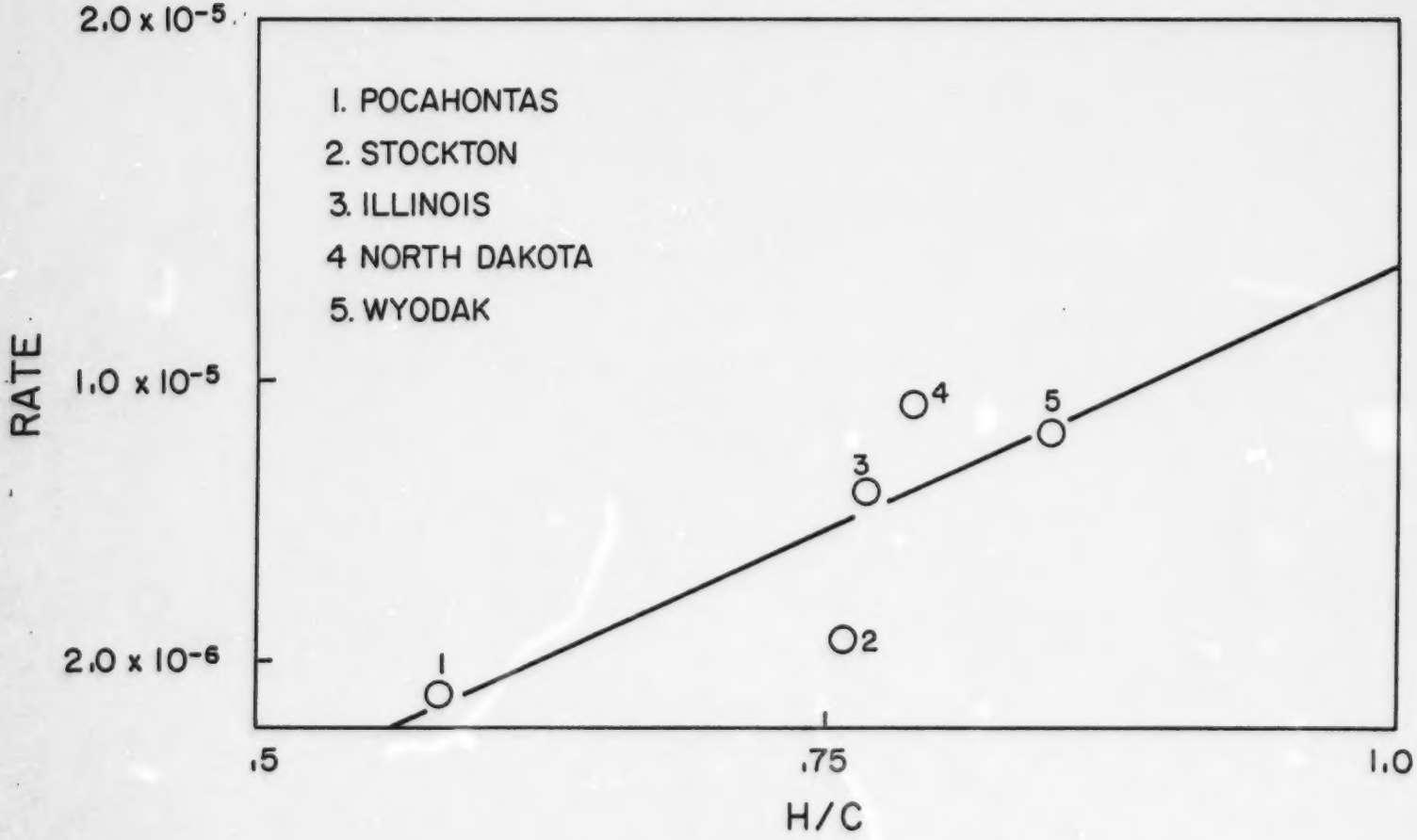
2.0 x 10-5
1.0 x 10-5
2.0 x 10-6
RATE
1. POCAHONTAS
2. STOCKTON
3. ILLINOIS
4 NORTH DAKOTA
5. WYODAK
1
2
3
4
5
.5
.75
1.0
H/C

Figure 23

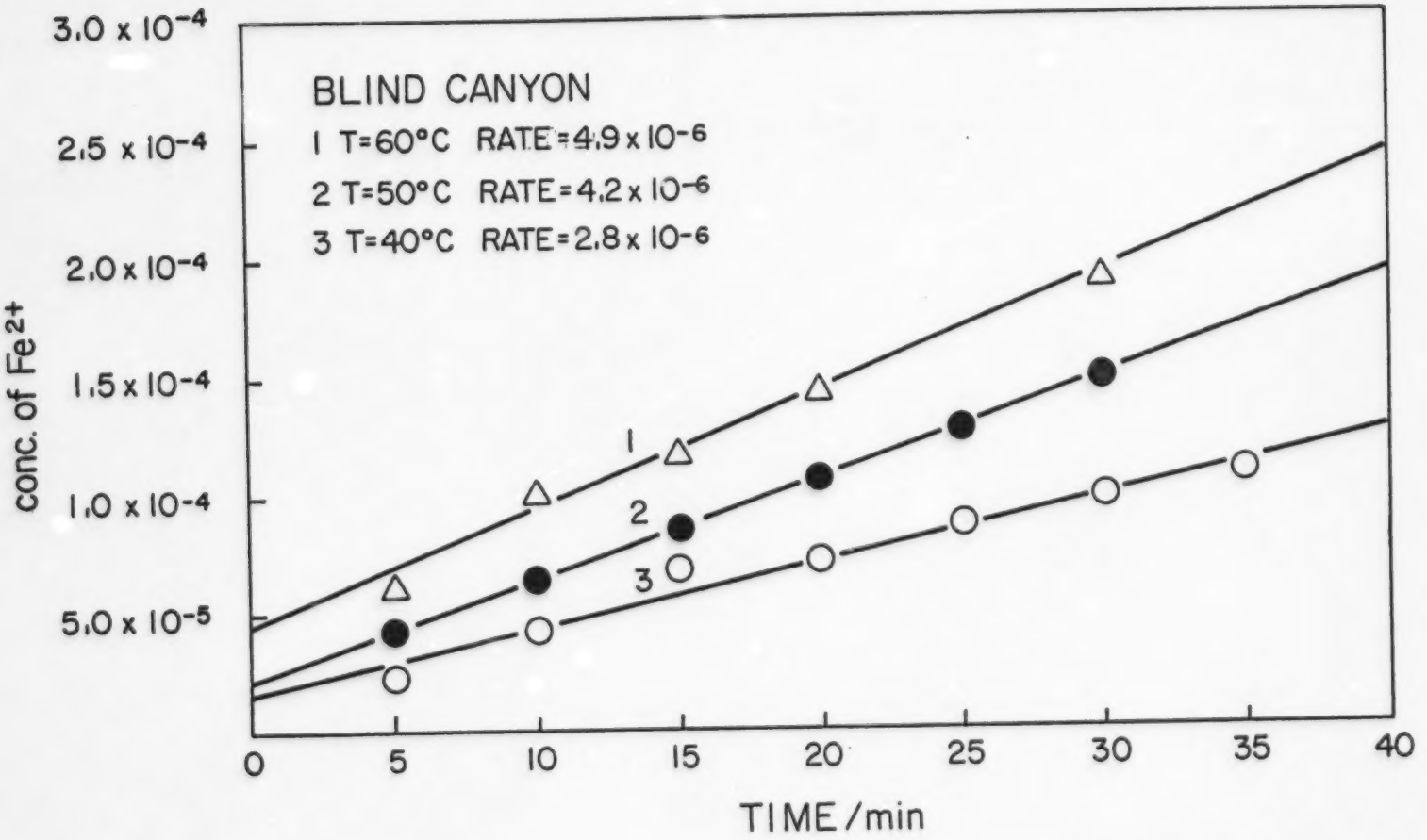
BLIND CANYON
1 T=60°C RATE=4.9 x 10-6
2 T=50°C RATE=4.2 x 10-6
3 T=40°C RATE=2.8 x 10-6
conc. of Fe2+
3.0 x 10-4
2.5 x 10-4
2.0 x 10-4
1.5 x 10-4
1.0 x 10-4
5.0 x 10-5
0
5
10
15
20
25
30
35
40
TIME/min
1
2
3

Figure 24

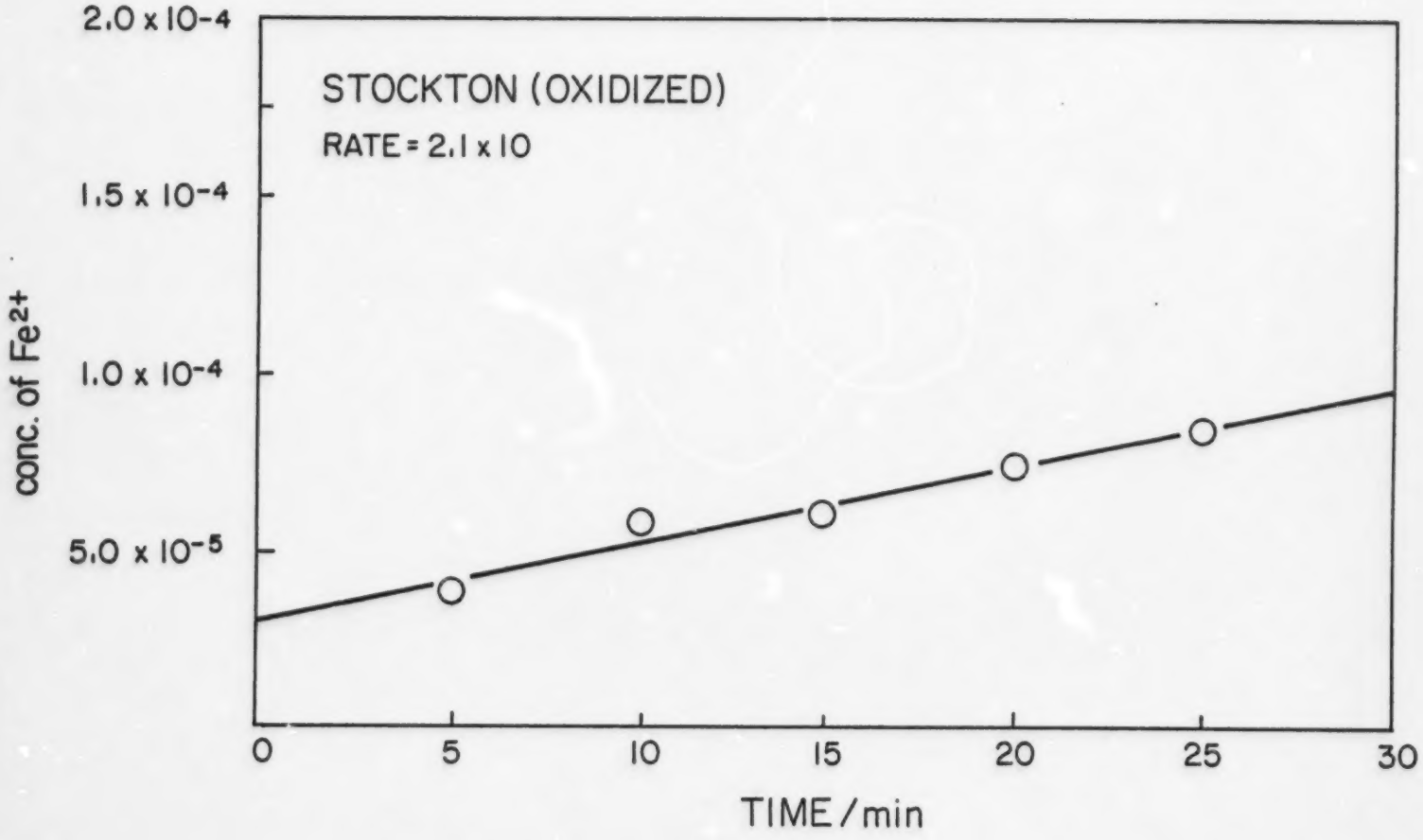
STOCKTON (OXIDIZED)
RATE = 2.1 x 10
2.0 x 10-4
1.5 x 10-4
1.0 x 10-4
5.0 x 10-5
conc. of Fe2+
0
5
10
15
20
25
30
TIME / min

Figure 25

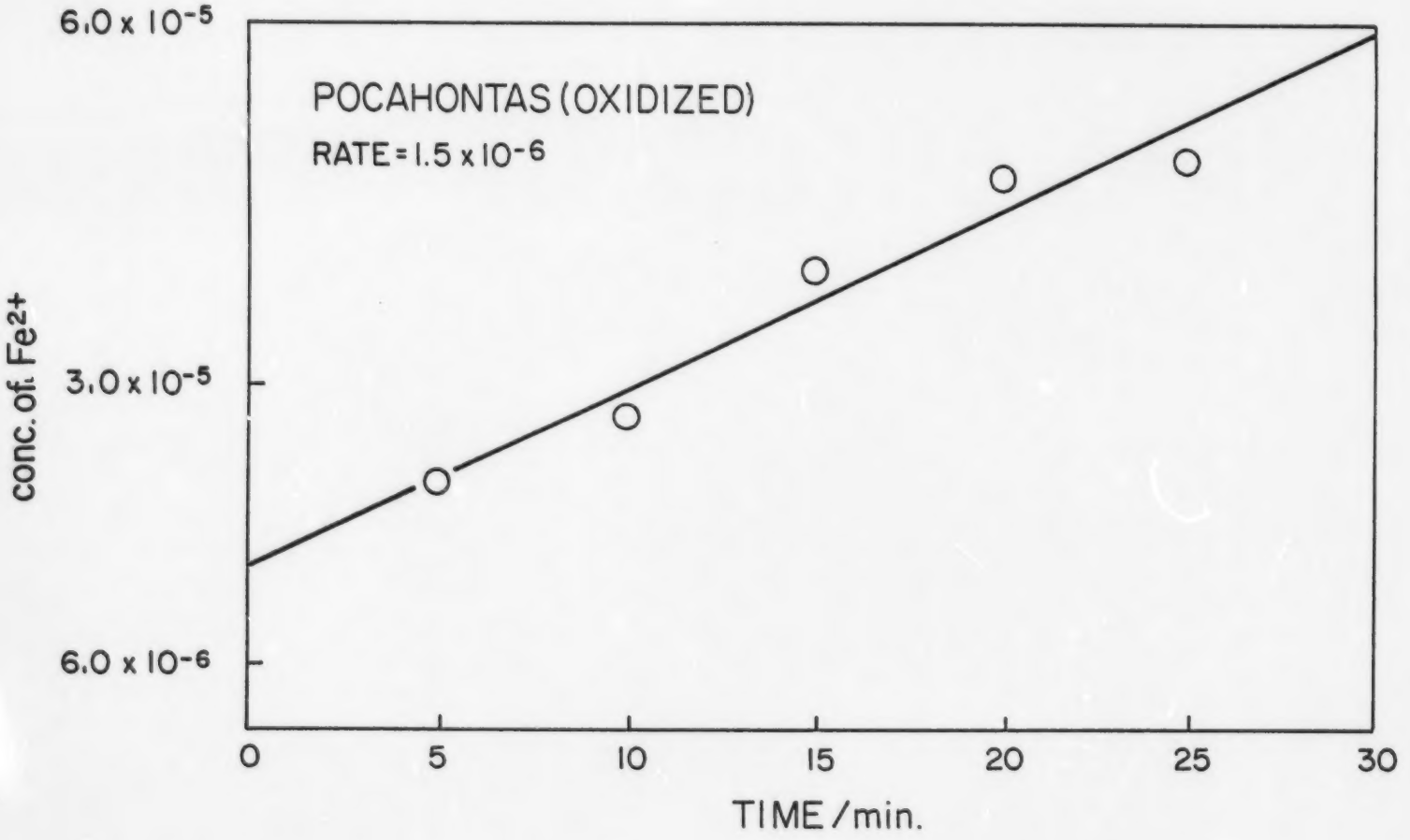
POCAHONTAS (OXIDIZED)
RATE = 1.5 x 10-6
6.0 x 10-5
3.0 x 10-5
6.0 x 10-6
conc. of Fe2+
0
5
10
15
20
25
30
TIME / min.

Figure 26

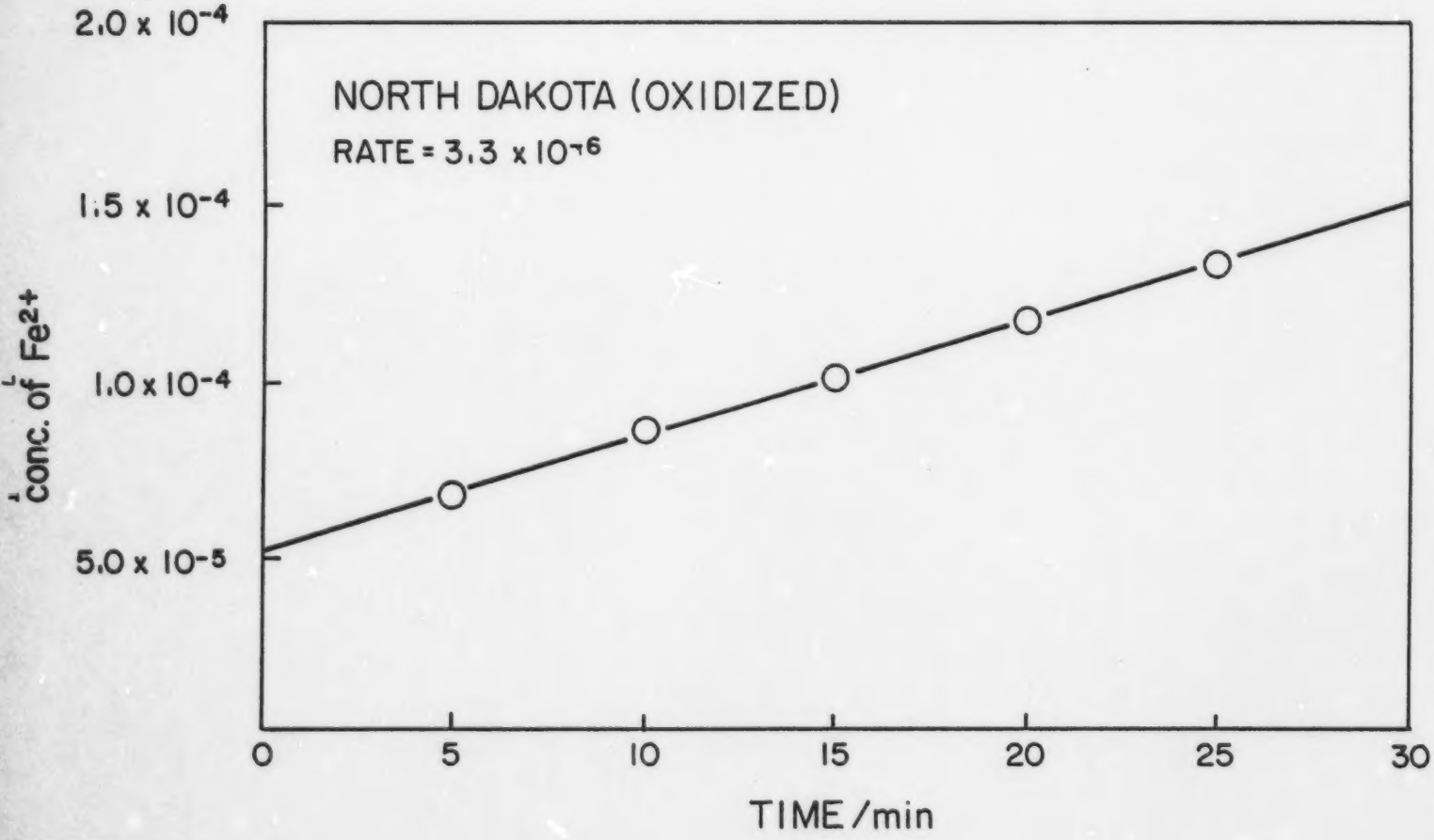
NORTH DAKOTA (OXIDIZED)
RATE = 3.3 x 10⁻⁶
2.0 x 10⁻⁴
1.5 x 10⁻⁴
1.0 x 10⁻⁴
5.0 x 10⁻⁵
conc. of Fe²⁺
0
5
10
15
20
25
30
TIME/min

Figure 27

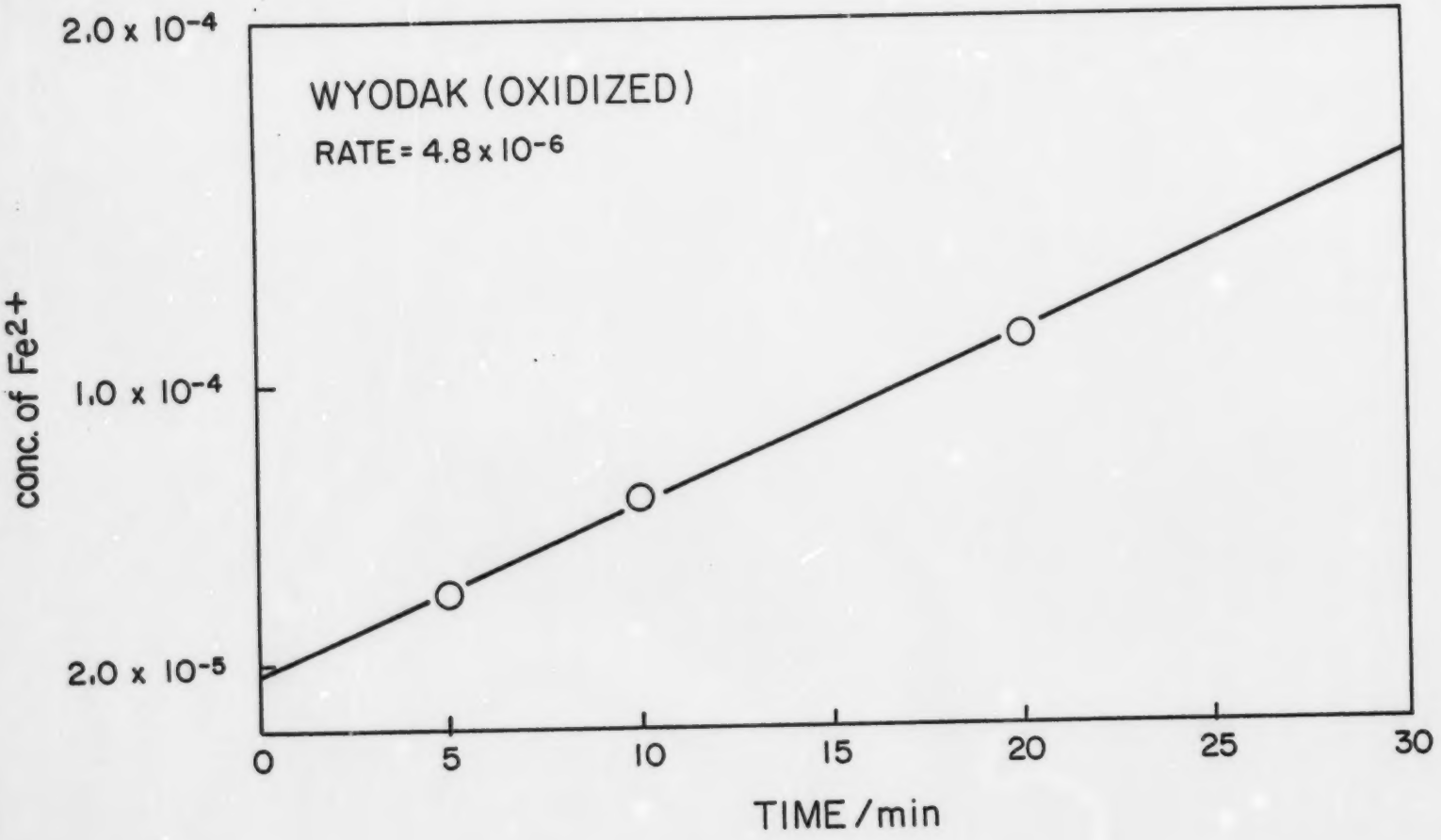
WYODAK (OXIDIZED)
RATE = 4.8 x 10-6
2.0 x 10-4
1.0 x 10-4
2.0 x 10-5
conc. of Fe2+
0
5
10
15
20
25
30
TIME / min

Figure 28

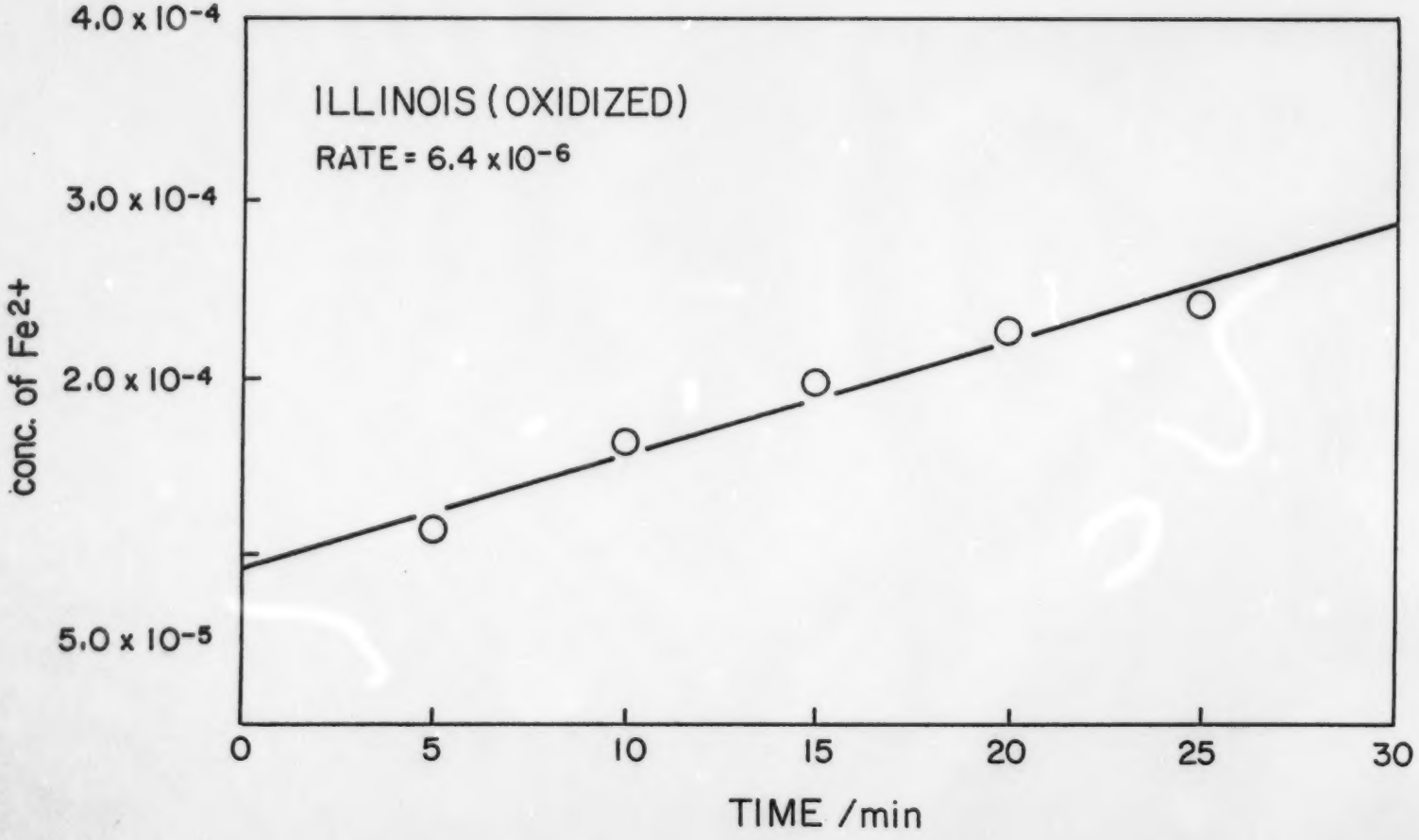
ILLINOIS (OXIDIZED)
RATE = 6.4 x 10-6
4.0 x 10-4
3.0 x 10-4
2.0 x 10-4
5.0 x 10-5
conc. of Fe2+
0
5
10
15
20
25
30
TIME /min

Figure 29

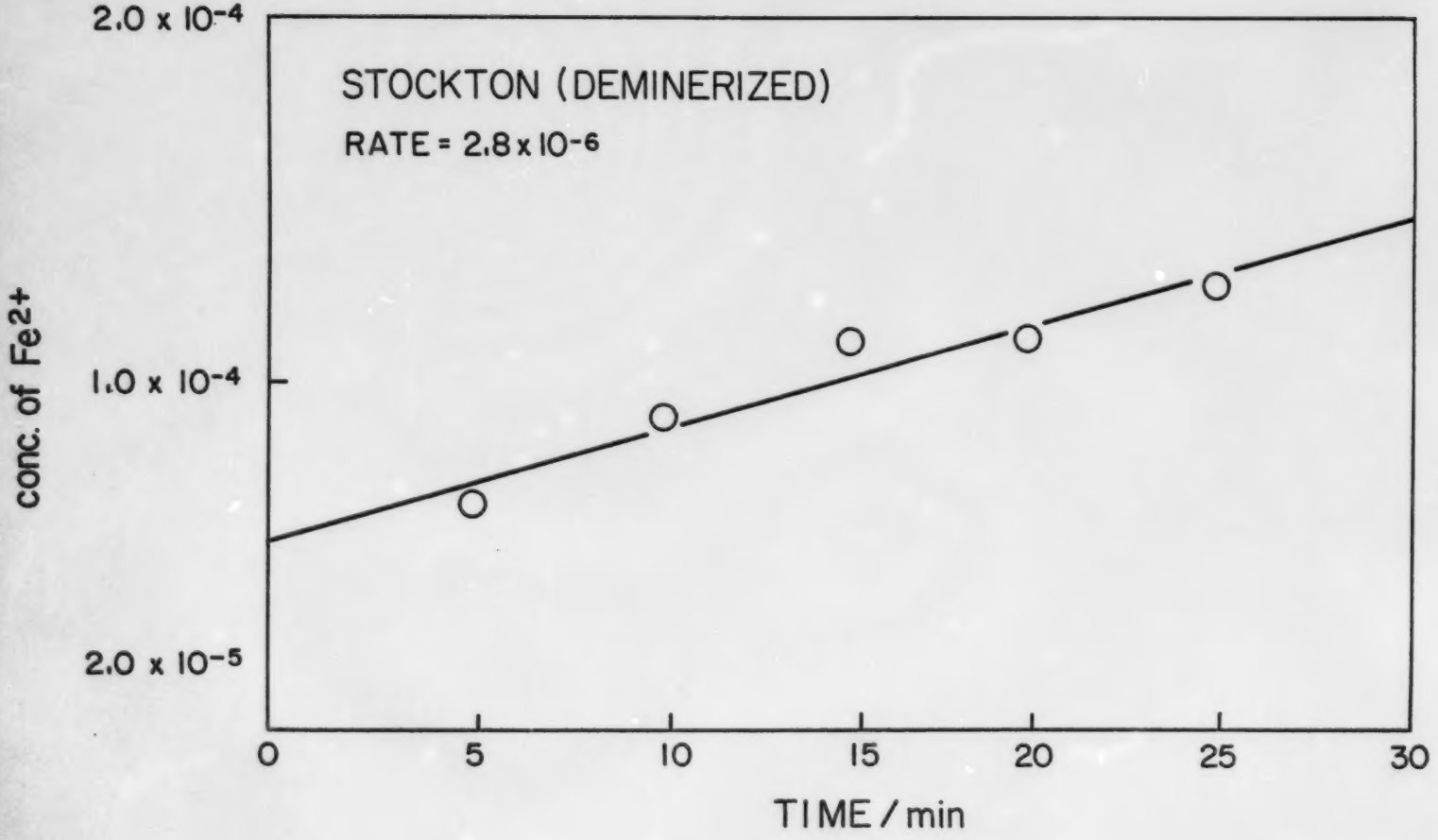
2.0 x 10-4
1.0 x 10-4
2.0 x 10-5
conc. of Fe2+
STOCKTON (DEMINERIZED)
RATE = 2.8 x 10-6
0
5
10
15
20
25
30
TIME / min

Figure 30

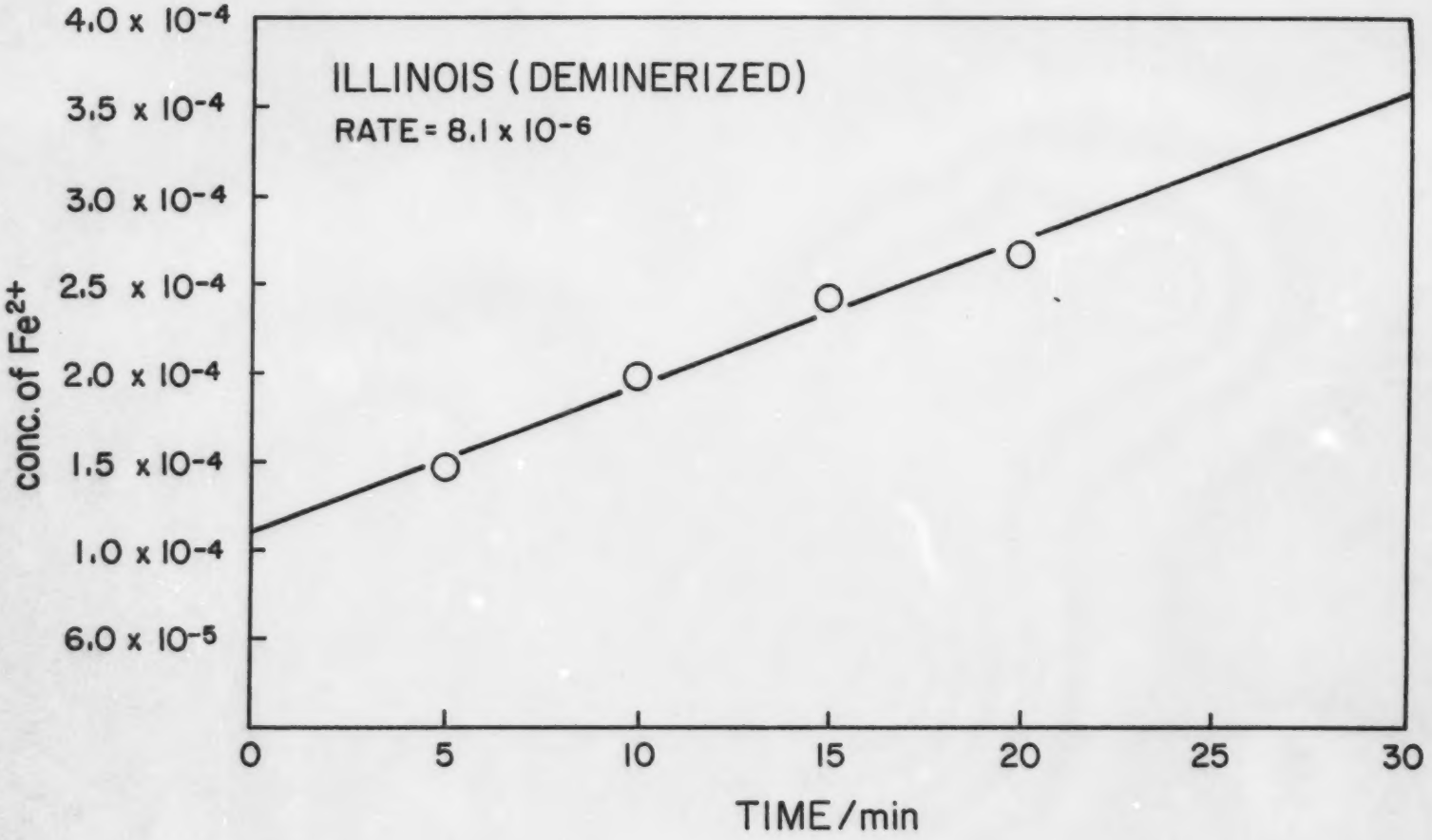
ILLINOIS (DEMINERIZED)
RATE = 8.1 x 10-6
conc. of Fe2+
4.0 x 10-4
3.5 x 10-4
3.0 x 10-4
2.5 x 10-4
2.0 x 10-4
1.5 x 10-4
1.0 x 10-4
6.0 x 10-5
0
5
10
15
20
25
30
TIME/min

Figure 31

GLOSSARY

XPS - X-ray Photoelectron Spectroscopy

SEM - Scanning Electron Microscopy

SIMS - Secondary Ion Mass Spectrometry

APPENDIX

	Ash	Volatile	%C	%H	%S	%N	%O
P804	19.8	31.5	67.1	4.3	1.9	0.7	6.3
P832	9.5	22.1	80.4	4.2	0.3	1.2	3.8
P851	4.4	35.7	82.0	5.1	1.7	1.6	4.4
KG15	36	-	-	-	-	-	-

Calculation of As-received and maf Values for APCSP Samples from Dry Data from CT&E

Coal	UF	WY	IL	PITT	POC	UT	WV	ND
AR H_2O	1.13	28.09	7.97	1.65	0.65	4.63	2.42	32.24
AR Ash	13.03	6.31	14.25	9.10	4.74	4.49	19.36	6.59
AR VM	27.14	32.17	36.86	37.20	18.48	43.72	29.44	30.45
AR S	2.29	0.45	4.45	2.15	0.66	0.59	0.69	0.54
AR Btu	13315	8426	10999	13404	14926	13280	11524	7454
Dry Ash	13.18	8.77	15.48	9.25	4.77	4.71	19.84	9.72
Dry VM	27.45	44.73	40.05	37.82	18.60	45.84	30.17	44.94
Dry S	2.32	0.63	4.83	2.19	0.66	0.62	0.71	0.80
Dry Btu	13467	11717	11951	13629	15024	13925	11810	11001
Dry C	74.23	68.43	65.65	75.50	86.71	76.89	66.20	65.85
Dry H	4.08	4.88	4.23	4.83	4.23	5.49	4.21	4.36
Dry N	1.35	1.02	1.16	1.49	1.27	1.50	1.25	1.04
Dry Cl	0.00	0.03	0.05	0.11	0.19	0.03	0.10	0.04
Dry F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pyritic S	1.77	0.17	2.47	1.32	0.15	0.24	0.16	0.14
Sulfate S	0.00	0.03	0.01	0.01	0.03	0.03	0.03	0.03
Organic S	0.64	0.43	2.01	0.81	0.48	0.35	0.52	0.63

Dmmf* Modified Parr Formula (used)
MM (dry) = 1.13 Ash + 0.47 Pyritic S (dry) + 0.50 Cl (dry)

Parr Formula (not used)
MM (dry) = 1.08 Ash (dry) + 0.55 S (total dry)

UF = Upper Freeport seam from Pennsylvania
WY = Wyodak-Anderson seam from Wyoming
IL = Herrin (Illinois #6) seam from Illinois
PITT = Pittsburgh (#8) seam from Pennsylvania
POC = Pocahontas (#3) seam from Virginia
UT = Blind Canyon seam from Utah
WV = Lewiston-Stockton seam from West Virginia
ND = Beulah Zap seam from North Dakota

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APPENDIX II

APPENDED TO:

IDENTIFICATION OF CHEMICALLY-SPECIFIC

REACTION SITES ON COAL SURFACES - PHASE II

BY

R.R. MARTIN

A REPORT FOR

CANMET/ENERGY RESEARCH LABORATORY

DEPARTMENT OF ENERGY, MINES & RESOURCES

OTTAWA, ONTARIO

FROM

THE DEPARTMENT OF CHEMISTRY

UNIVERSITY OF WESTERN ONTARIO

LONDON, ONTARIO

DSS CONTRACT SERIAL NUMBER 23440-8-9076/01-SS

CANMET SCIENTIFIC AUTHORITY: DR. J.A. M^{AC}PHEE

Introduction:

We have shown (Chapter 5) that coal reduces Fe^{3+} and that the reaction can be followed colorimetrically if $K_3Fe(CN)_6$ is added to solutions of $FeCl_3$ that have been in contact with coal. The data were obtained by extracting solutions from the coal slurries at five minute intervals for 25 minutes. The data obtained showed:

1. Colored solutions were obtained because of the formation of the charge transfer complex $(Fe^{2+}/Fe^{3+})(CN)_6$, thus the rate of Fe^{3+} reduction could be followed colorimetrically.
2. The rate of coal oxidation was proportional to the O/C ratio for the coal.
3. The rate of reaction was unaffected by demineralization of the coal using HCl.
4. The overall rate of reaction was not affected if the coal was pre-oxidized by exposure to air at 108°C for five days.
5. There was strong evidence for an initial fast reaction between 0 - 5 minutes.
6. Very little reaction was observed if $K_3 Fe(CN)_6$ was added directly to the coal slurry. This is believed to be due to strong adsorption of CN^- on reactive sites on the coal surface.

The work reported in this section confirms adsorption of CN^- and investigates both the initial fast reduction of Fe^{3+} and a second slower reaction.

Experimental

Coal slurries were prepared as in chapter 5 using five Argonne Premium Coals. A single sample was isolated and $K_3Fe(CN)_6$ was added directly to the slurry with

$FeCl_3$ infrared spectra were obtained from the coal in KBr discs before and after this procedure.

Five samples of 100 mesh argonne premium coal were treated as before, solution was withdrawn from the slurry using a syringe with a filter at one minute intervals for the first five minutes and at five minute intervals for a total of twenty-five minutes. $K_3Fe(CN)_6$ was added to the solution and the concentration of Fe^{2+} was calculated from the absorbance observed at 700 nm. One sample was used to obtain X-ray photoelectron spectra (XPS) of the surface iron following exposure of the coal to the $FeCl_3$ solution.

Five additional samples were oxidized by exposure to air at 105°C for five days and the rate of reduction of Fe^{3+} was measured as before.

Results and Discussion

The IR spectra of the coal surface before and after exposure to $K_3Fe(CN)_6$ is shown in figure 32. The appearance of a strong C ≡ N vibration line after exposure to CN^- in solution confirms our hypothesis that CN adsorption blocks reactive sites and prevents surface reaction with Fe^{3+}.

The XPS data show a set of iron oxidation states including Fe_3O_4 (708.3 ev), Fe_2O_3 (711.1 ev) and FeO (709.5 ev), figure 33. These results provide direct evidence for reduced iron on the coal surface and coupled with the formation of prussian blue account for the suite of colors observed by Salehi and Hamilton[19].

The kinetic data for both fresh and oxidized coal are shown in figures 34-38. Table 1 gives the rate of reaction for the first, fast reaction, before and after oxidation obtained by estimating the slope between 1 and 3 minutes to avoid forcing the initial point through zero.

Table 2 gives the rate of reaction for the slow step using the slope between 10 and 20 minutes. After 20 minutes the reaction appears to be substantially complete. We have used this simple approach to approximate the two rates. The data can not be fitted satisfactorally to either single first order or second order kinetics. More elaborate fitting, such as the sum of two first order processes is not likely to yield physically meaningful results both because of the large number of parameters involved and the limited data obtained.

The results show two distinct processes, the first dominates during the first five minutes of the reaction second from then till around 25 minutes. In both cases the reaction is a rate is strongly correlated to the O/C ratio of the coal. The effect of oxidation is striking, the initial reaction is essentially unaffected in the coals of lowest O/C where the initial reaction is comparatively slow in any case, and is strongly suppressed in coals of high O/C, where the initial reaction is an order of magnititude faster, while the slow process is hardly affected in any case. The results suggest that there is a group of reactive sites which are responsible for the rapid reduction of Fe^{3+} in all the coals studied and that the concentration of these sites in the coal increases with O/C. In addition these sites are oxidized by exposure to air at 105°C and are replaced by less reactive functional groups. The slow reaction is due either to less reactive species which are resistant to air oxidation or to a diffusion controlled process that prevents the Fe^{3+} from reaching reactive sites rapidly. The first of these explanations is in better agreement with the virtual elimination of the fast reaction by mild air oxidation. Electrochemical data suggests that a significant number of the organic species present in coal[21] (for instance hydroquinone-like species and aromatic structures containing basic nitrogen) provide a series of sites with varying oxidation potentials. The results are consistent with a model in which coal contains organic functional

groups which reduce Fe^{3+} more or less readily. The concentration of these species is a function of the O/C ratio in the parent coal. In all the coals studied the more reactive of these groups are sensitive to air oxidation which markedly inhibits Fe^{3+} reduction. The less reactive material is resistant to air oxidation and is responsible for the slow reduction of Fe^{3+}.

Conclusions

The net reaction leading to the reduction of Fe^{3+} by coal is composed of two components the first, which is significantly more rapid than the second is largely complete after five minutes. The second appears close to completion after 25 minutes.

The kinetics of both reaction regions is a function of the O/C ratio of the parent coal. The species responsible for the fast reaction is readily destroyed by low temperature air oxidation. The slow reaction is relatively insensitive to similar oxidation conditions.

Electrochemical data suggests that oxygen function groups resembling hydroquinone would be oxidized by Fe^{3+}, a range of similar compounds of systematically varying oxidation potentials is consistent with the results presented.

The kinetics of the Fe^{3+} reduction provide a simple and rapid test of coal reactivity.

Additional reference.

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Table 1

Fe^{3+} Reduction Rate 0 - 5 Minutes

Coal	O/C	Rate Fresh $\times 10^{-5}$ $ML^{-1}min^{-1}$	Rate Oxidized $\times 10^{-5}$ $ML^{-1}min^{-1}$
Pocahontas (POC)	0.038	0.4	0.5
Stockton (WV)	0.10	1.3	0.73
Illinois #6 (IL)	0.14	4.3	3.9
Wyodak (WY)	0.26	5.3	2.6
North Dakota (ND)	0.29	8.0	0.9

Table 2

Fe^{3+} Reduction Rate 5 - 25 Minutes

Coal	O/C	Rate Fresh $\times 10^{-5}$ $ML^{-1}min^{-1}$	Rate Oxidized $\times 10^{-5}$ $ML^{-1}min^{-1}$
Pocahontas (POC)	0.038	0.3	0.2
Stockton (WV)	0.10	0.3	0.2
Illinois #6 (IL)	0.14	0.9	0.6
Wyodak (WY)	0.26	1.0	1.4
North Dakota (ND)	0.29	0	1.4

APPENDII.FUE

FIGURE 33

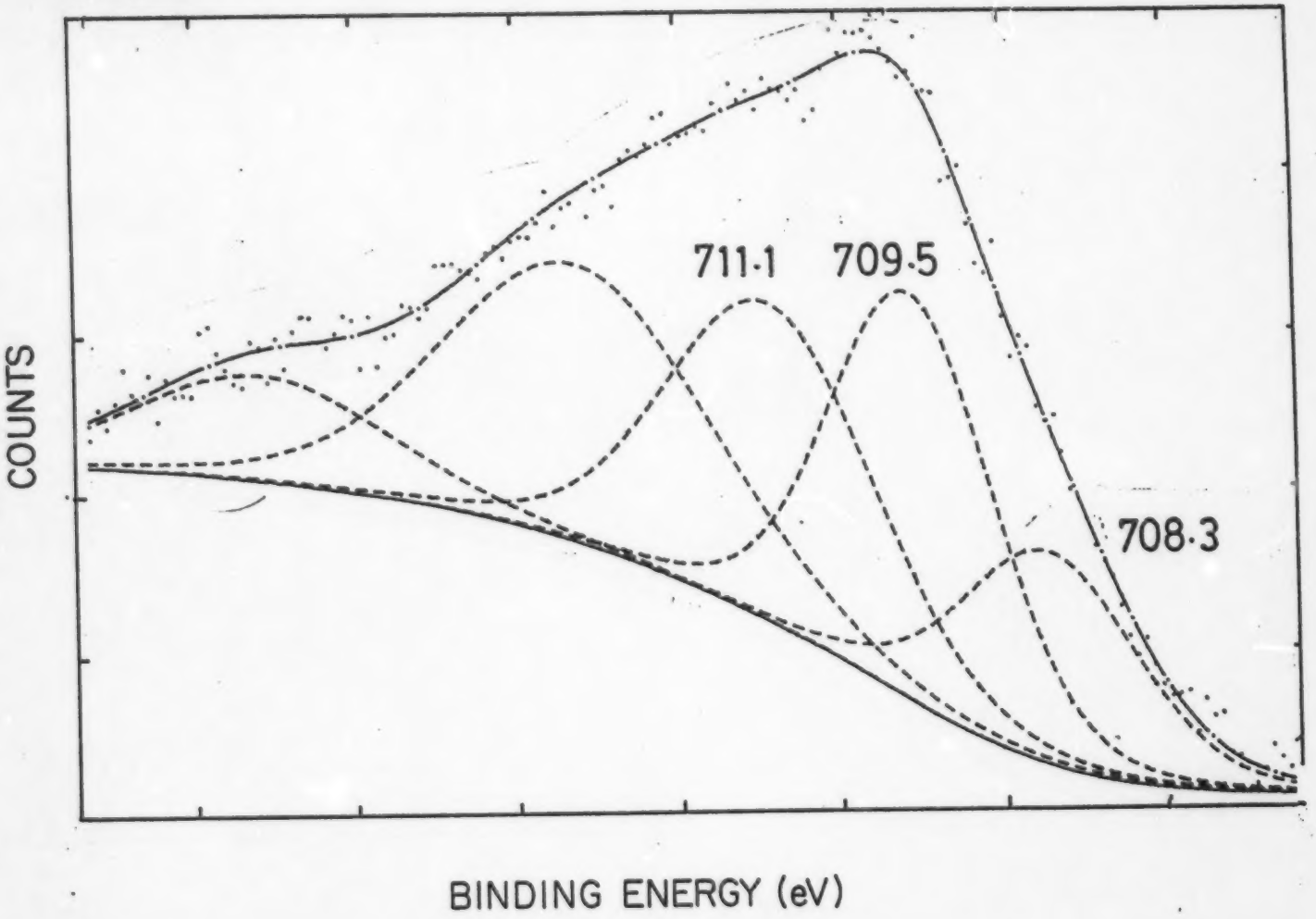

FIGURE 33: X-RAY PHOTOELECTRON SPECTRUM OF COAL SURFACE AFTER EXPOSURE TO Fe^{3+} SLURRY.

FIGURE 32

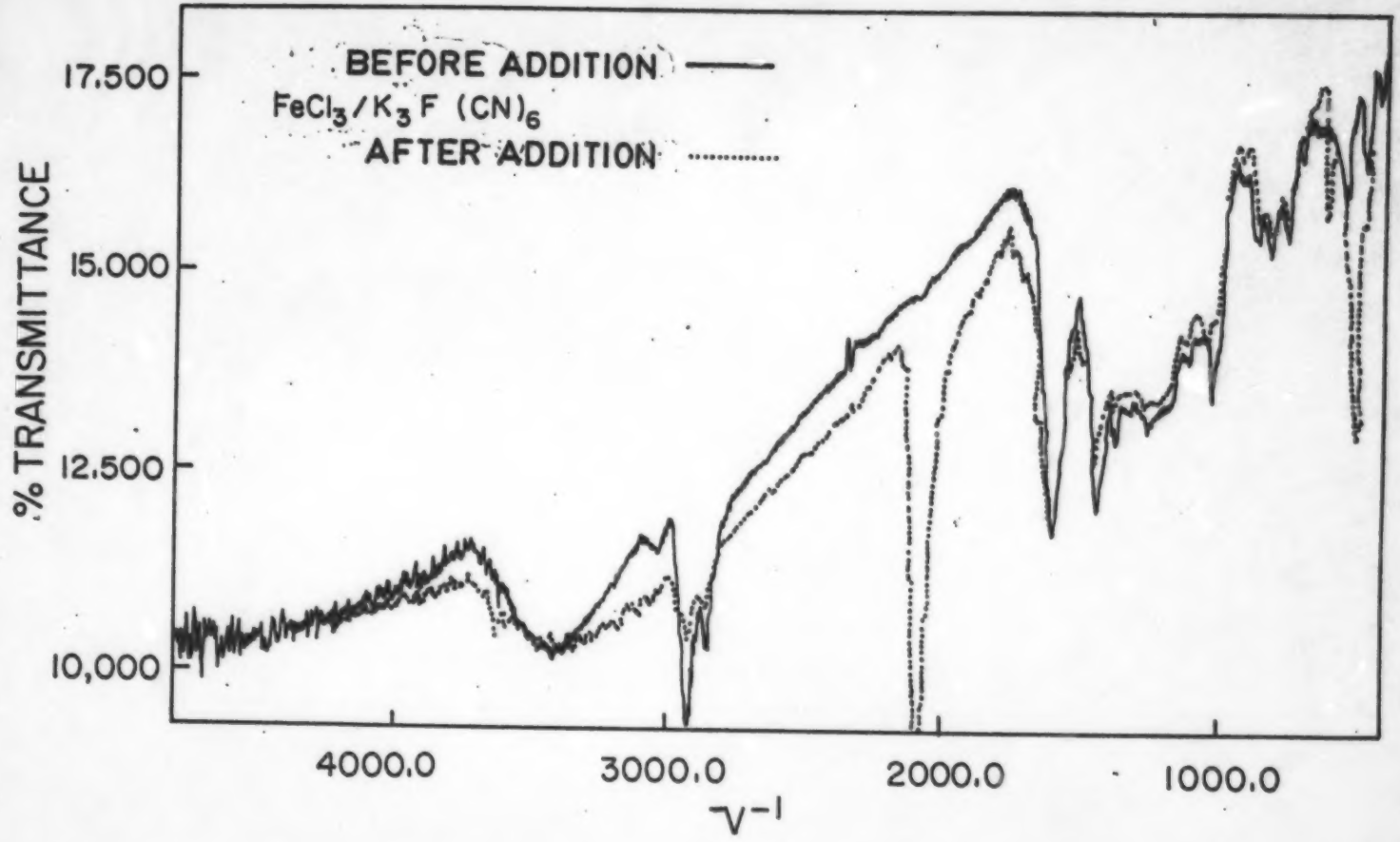

FIGURE 32: INFRA-RED SPECTRUM OF COAL SURFACE BEFORE AND AFTER EXPOSURE TO $K_3Fe(CN)_6$ IN SLURRY.

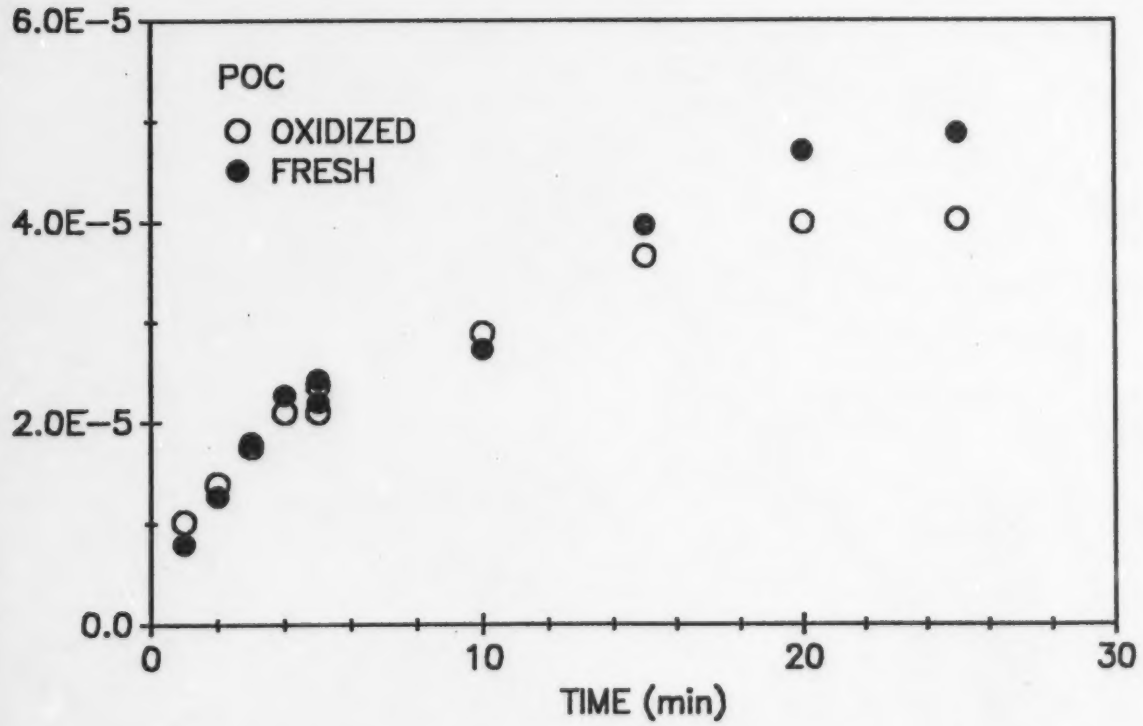

FIGURE 34: $[Fe^{2+}]$ 'NO TIME FOR POCAMONTAS COAL.

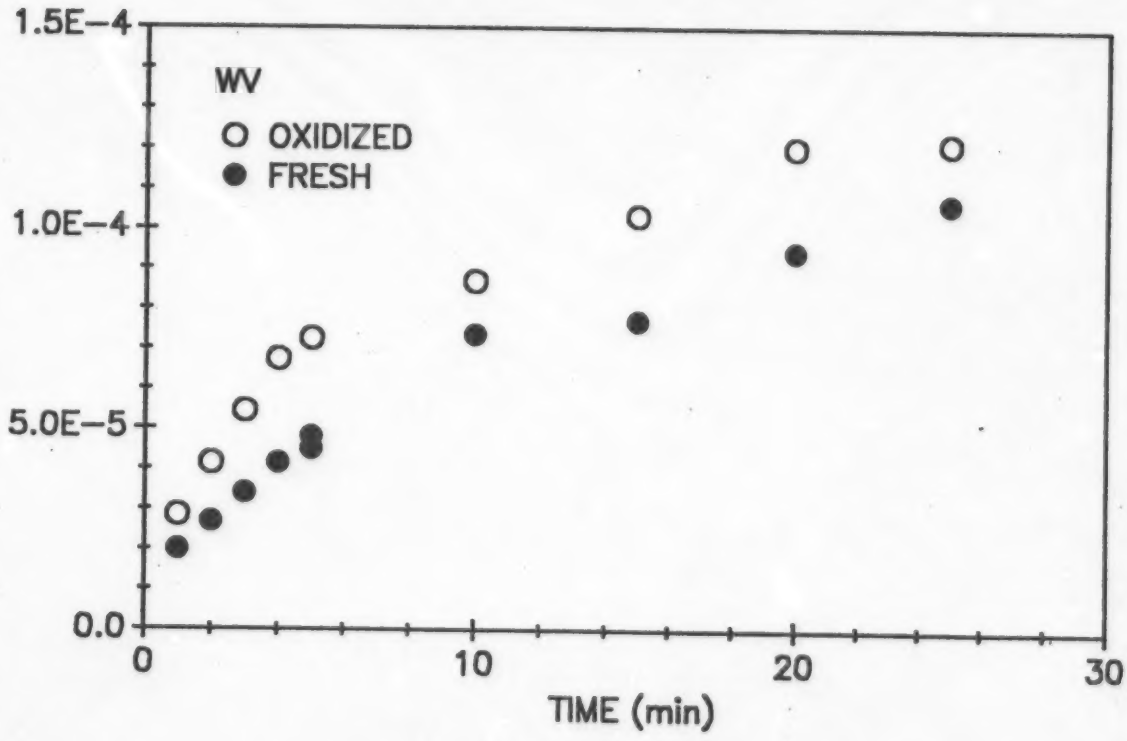

FIGURE 35: $[Fe^{2+}]$ NO TIME FOR STOCKTON COAL.

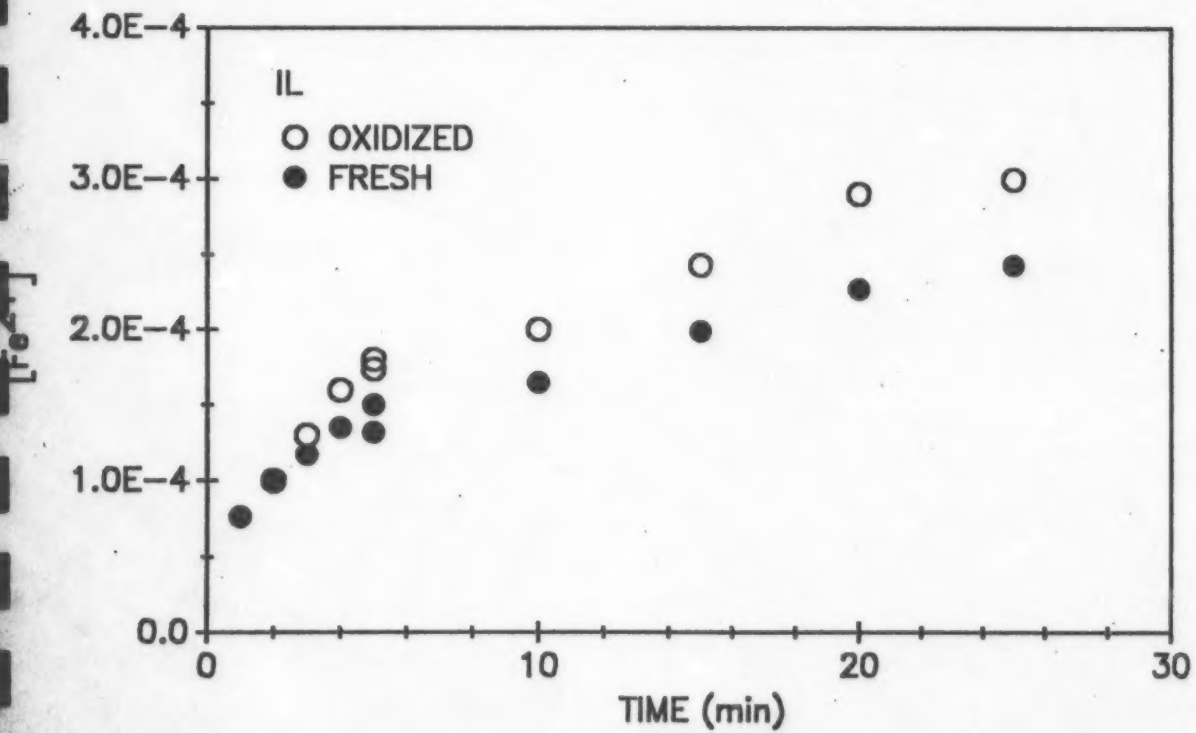

FIGURE 36: [Fe^{2+}] NO TIME FOR ILLINOIS #6 COAL.

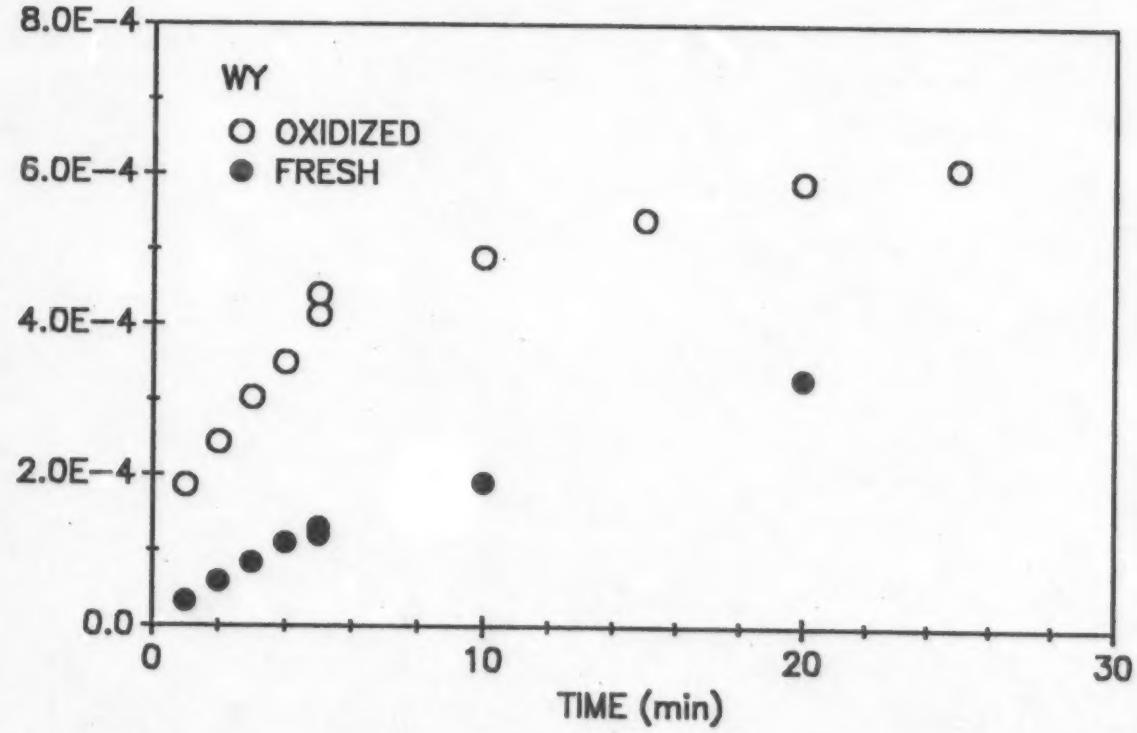

FIGURE 37: $[Fe^{2+}]$ NO TIME FOR WYODAK COAL.

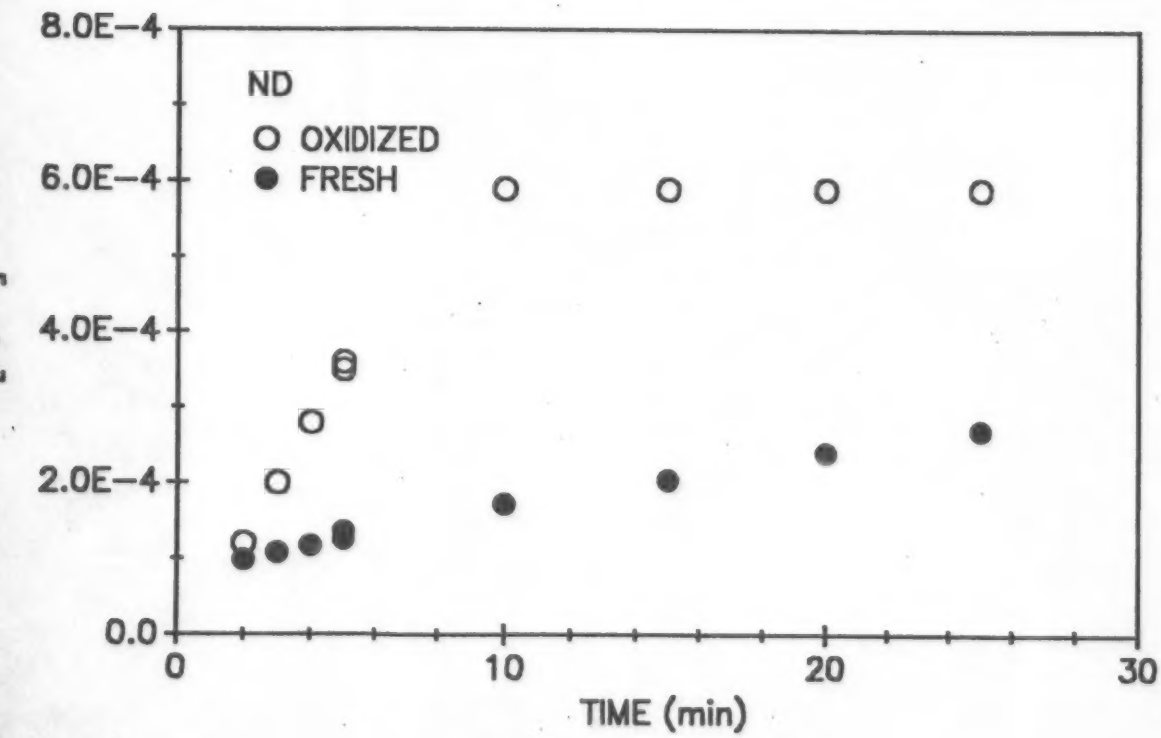

FIGURE 35: $[Fe^{2+}]$ NO TIME FOR NORTH DAKOTA COAL.